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(54) **LOW VISCOSITY LUBRICATING OIL BASE STOCKS AND PROCESSES FOR PREPARING SAME**

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(51) **Int. Cl.**

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| ***C10M 107/46*** | (2006.01) |
| ***C10M 105/36*** | (2006.01) |
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| ***C07C 323/52*** | (2006.01) |
| ***C10M 135/26*** | (2006.01) |

(52) **U.S. Cl.**

CPC ............ ***C10M 105/72*** (2013.01); ***C07C 321/14*** (2013.01); ***C07C 323/52*** (2013.01); ***C10M 135/26*** (2013.01); *C10M 2203/1006* (2013.01); *C10M 2203/1025* (2013.01); *C10M 2205/0285* (2013.01); *C10M 2205/173* (2013.01); *C10M 2219/081* (2013.01); *C10M 2219/085* (2013.01); *C10N 2220/022* (2013.01); *C10N 2230/02* (2013.01); *C10N 2230/74* (2013.01); *C10N 2270/00* (2013.01)

(58) **Field of Classification Search**

USPC ................................................ 508/465, 517

See application file for complete search history.

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(57) **ABSTRACT**

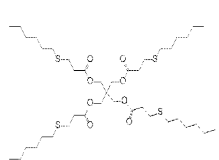
A composition that includes one or more compounds represented by the formula

$$(R_1)_a(X)(R_2)_b$$

wherein $R_1$ and $R_2$ are the same or different and are the residue of an alkyl group having from 4 to 40 carbon atoms, X is the residue of an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, a is a value from 1 to 6, and b is a value from 0 to 6. The composition has a viscosity ($Kv_{100}$) from 2 to 30 at 100° C., a viscosity index (VI) from 100 to 200, and a Noack volatility of no greater than 20 percent. The disclosure also relates to a process for producing the composition, a lubricating oil base stock and lubricating oil containing the composition, and a method for improving one or more of solubility and dispersancy of polar additives in a lubricating oil by using as the lubricating oil a formulated oil containing the composition.

**19 Claims, 1 Drawing Sheet**

I



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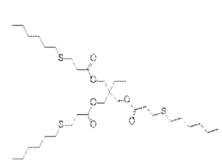

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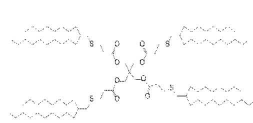

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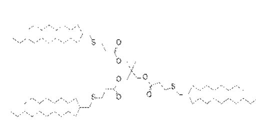

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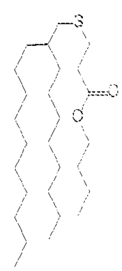

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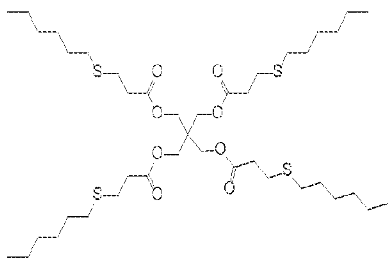

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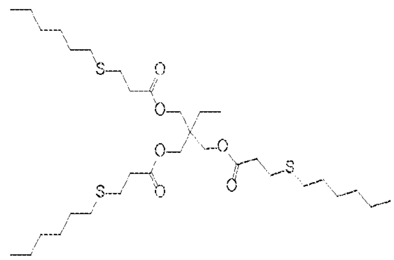

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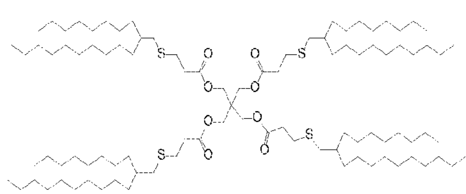

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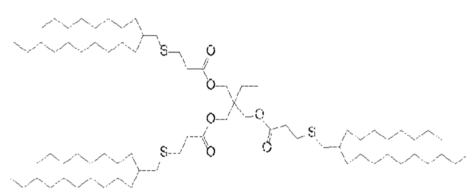


V

# LOW VISCOSITY LUBRICATING OIL BASE STOCKS AND PROCESSES FOR PREPARING SAME

## FIELD

This disclosure relates to low viscosity, low volatility compositions that include one or more heteroatom-containing, aliphatic, aromatic or cycloaliphatic hydrocarbon compounds, a process for producing the compositions, a lubricating oil base stock and lubricating oil containing the composition, and a method for improving one or more of solubility and dispersancy of polar additives in a lubricating oil by using as the lubricating oil a formulated oil containing the composition.

## BACKGROUND

Lubricants in commercial use today are prepared from a variety of natural and synthetic base stocks admixed with various additive packages and solvents depending upon their intended application. The base stocks typically include mineral oils, polyalphaolefins (PAO), gas-to-liquid base oils (GTL), silicone oils, phosphate esters, diesters, polyol esters, and the like.

A major trend for passenger car engine oils (PCEOs) is an overall improvement in quality as higher quality base stocks become more readily available. Typically the highest quality PCEO products are formulated with base stocks such as PAOs or GTL stocks.

PAOs and GTL stocks are an important class of lube base stocks with many excellent lubricating properties, including high viscosity index (VI) but have low polarity. This low polarity leads to low solubility and dispersancy for polar additives or sludge generated during service. These base stocks require the use of cobase stocks to improve additive and deposit solubility.

Therefore, there is a, need for polar cobase fluids that provide appropriate solubility and dispersibility for polar additives or sludge generated during service of lubricating oils.

The present disclosure also provides many additional advantages, which shall become apparent as described below.

## SUMMARY

This disclosure relates in part to a composition comprising one or more compounds represented by the formula

$$(R_1)_a(X)(R_2)_b$$

wherein $R_1$ and $R_2$ are the same or different and are the residue of an alkyl group having from 4 to 40 carbon atoms, X is the residue of an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, a is a value from 1 to 6, and b is a value from 0 to 6. The composition has a viscosity ($Kv_{100}$) from 2 to 30 at 100° C., and a viscosity index (VI) from 100 to 200.

This disclosure also relates in part to a composition comprising one or more heteroatom-containing hydrocarbon compounds. The one or more heteroatom-containing hydrocarbon compounds are produced by a process comprising reacting a polyalphaolefin oligomer or α-olefin ($C_4$-$C_{40}$) with an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, optionally in the presence of a catalyst,



under reaction conditions sufficient to produce the one or more heteroatom-containing hydrocarbon compounds.

This disclosure further relates in part to a process for producing a composition comprising one or more heteroatom-containing hydrocarbon compounds. The process comprises reacting a polyalphaolefin oligomer or a α-olefin ($C_4$-$C_{40}$) with an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, optionally in the presence of a catalyst, under reaction conditions sufficient to produce the composition.

This disclosure yet further relates in part to a lubricating oil base stock comprising one or more compounds represented by the formula

$$(R_1)_a(X)(R_2)_b$$

wherein $R_1$ and $R_2$ are the same or different and are the residue of an alkyl group having from 4 to 40 carbon atoms, X is the residue of an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, a is a value from 1 to 6, and b is a value from 0 to 6. The composition has a viscosity ($Kv_{100}$) from 2 to 30 at 100° C., a viscosity index (VI) from 100 to 200, and a Noack volatility of no greater than 20 percent.

This disclosure also relates in part to a lubricating oil comprising a lubricating oil base stock as a major component, and a heteroatom-containing hydrocarbon cobase stock as a minor component. The heteroatom-containing hydrocarbon cobase stock comprises one or more compounds represented by the formula

$$(R_1)_a(X)(R_2)_b$$

wherein $R_1$ and $R_2$ are the same or different and are the residue of an alkyl group having from 4 to 40 carbon atoms, X is the residue of an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, a is a value from 1 to 6, and b is a value from 0 to 6. The composition has a viscosity ($Kv_{100}$) from 2 to 30 at 100° C., a viscosity index (VI) from 100 to 200, and a Noack volatility of no greater than 20 percent.

This disclosure further relates in part to a method for improving one or more of solubility and dispersancy of polar additives in a lubricating oil by using as the lubricating oil a formulated oil comprising a lubricating oil base stock as a major component, and a heteroatom-containing hydrocarbon cobase stock as a minor component. The heteroatom-containing hydrocarbon cobase stock comprises one or more compounds represented by the formula

$$(R_1)_a(X)(R_2)_b$$

wherein $R_1$ and $R_2$ are the same or different and are the residue of an alkyl group having from 4 to 40 carbon atoms, X is the residue of an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, a is a value from 1 to 6, and b is a value from 0 to 6. The composition has a viscosity ($Kv_{100}$) from 2 to 30 at 100° C., a viscosity index (VI) from 100 to 200, and a Noack volatility of no greater than 20 percent.

In addition to improved solubility and dispersibility for polar additives and/or sludge generated during service of lubricating oils, improved fuel efficiency can also be attained in an engine lubricated with a lubricating oil by using as the lubricating oil a formulated oil in accordance with this disclosure. The formulated oil comprises a lubricating oil base stock as a major component, and a heteroatom-containing, aliphatic, aromatic or cycloaliphatic hydrocarbon cobase stock as a minor component. The lubricating oils of this disclosure are particularly advantageous as passenger vehicle engine oil (PVEO) products.

Further objects, features and advantages of the present disclosure will be understood by reference to the following drawings and detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** depicts a synthetic base stock (I) formed by the reaction of vinylidene double bond terminated 1-decene dimer and 3-mercaptopropionate of Example 3, a synthetic base stock (II) formed by the reaction of pentaerythritoltetrakis(3-mercaptopropionate) with 1-hexene of Example 4, a synthetic base stock (III) formed by the reaction of trimethylopropanetris(3-mercaptopropionate) with 1-hexene of Example 5, a synthetic base stock (IV) formed by the reaction of pentaerythritoltetrakis(3-mercaptopropionate) with mPAO dimer of Example 6, and a synthetic base stock (V) formed by the reaction of trimethylopropanetris(3-mercaptopropionate) with mPAO dimer of Example 7.

DETAILED DESCRIPTION

All numerical values within the detailed description and the claims herein are modified by "about" or "approximately" the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

In an embodiment, this disclosure relates to ester or acid containing thiol or ester or acid containing polythiol and aliphatic, aromatic or cycloaliphatic polythiol (e.g., 1,2-ethanedithiol) containing Low Viscosity Low Volatility (LVLV) sulfur containing synthetic base stocks. The double bond terminated alkanes as prepared by $\alpha$-olefin dimerization or ethylene oligomerization are reacted with these various thiols or polythiols to obtain synthetic base stocks. The products exhibit good lubricant properties.

In another embodiment, this disclosure relates to oxygen and sulfur heteroatom containing Group V synthetic base stocks. The double bond terminated alkanes as prepared by either ethylene oligomerization or via $\alpha$-olefin dimerization are reacted with ester or acid containing thiol or polythiol to obtain synthetic base stocks. Illustrative synthetic base stocks prepared from ester or acid containing thiols and polythiols are depicted in FIG. **1**.

The compositions of this disclosure possess low viscosity, low Noack volatility and superior low temperature properties. The compositions of this disclosure exhibit excellent bulk flow properties with built-in polarity.

As indicated above, the compositions of this disclosure comprise one or more compounds represented by the formula

$$(R_1)_a(X)(R_2)_b$$

wherein $R_1$ and $R_2$ are the same or different and are the residue of an alkyd group having from 4 to 40 carbon atoms, X is the residue of an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, a is a value from 1 to 6, and b is a value from 0 to 6. The composition has a viscosity ($Kv_{100}$) from 2 to 30 at 100° C., and a viscosity index (VI) from 100 to 200. As used herein, viscosity ($Kv_{100}$) is determined by ASTM D 445-01, and viscosity index (VI) is determined by ASTM D 2270-93 (1998).

The compositions of this disclosure have a Noack volatility of no greater than 20 percent, preferably no greater than 18 percent, and more preferably no greater than 15 percent. As used herein, Noack volatility is determined by ASTM D-5800.

Illustrative $R_1$ and $R_2$ substituents include, for example, $C_{40}$ alkane hydrocarbons, the residue of mPAO dimers ($C_6$-$C_{40}$), trimers ($C_6$-$C_{40}$), tetramers ($C_6$-$C_{40}$) and higher oligomers, pentamer, hexamer, and the like, or $\alpha$-olefin ($C_6$-$C_{40}$). Preferably, $R_1$ and $R_2$ independently are the residue of a mPAO trimer, more preferably a mPAO dimer ($C_{12}$, $C_{16}$, $C_{20}$, $C_{24}$ or $C_{28}$). Illustrative X substituents include, for example, the residue of 1,2-ethanedithiol, 3-mercaptopropionate, pentaerythritoltetrakis(3-mercaptopropionate), trimethylopropanetris(3-mercaptopropionate), and the like.

Illustrative compositions of this disclosure include, for example, heteroatom-containing mPAO dimers, trimers, tetramers, pentamers, hexamers, and higher oligomers, or $\alpha$-olefin ($C_4$-$C_{40}$). Preferred compositions result from selective coupling of mPAO dimer (e.g., mPAO 1-decene) with an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol to form trimer analogues with a polar heteroatom, e.g., sulfur and/or oxygen.

In particular, compositions of this disclosure include, for example, the reaction product of vinylidene double bond terminated 1-octene dimer and 1,2-ethanedithiol, reaction of vinylidene double bond terminated 1-decene dimer and 1,2-ethanedithiol, reaction of vinylidene double bond terminated 1-decene dimer and 3-mercaptopropionate, reaction of pentaerythritoltetrakis(3-mercaptopropionate) with 1-hexene, reaction of trimethylopropanetris(3-mercaptopropionate) with 1-hexene, reaction of pentaerythritoltetrakis(3-mercaptopropionate) with mPAO dimer, reaction of trimethylopropanetris(3-mercaptopropionate) with mPAO dimer, and the like. Illustrative compositions prepared in accordance with this disclosure are depicted in FIG. **1**.

The composition of this disclosure can be prepared by a process that involves reacting a polyalphaolefin oligomer or alkyl olefin with an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol. The reaction is carried out optionally in the presence of a catalyst. The reaction is also carried out under reaction conditions sufficient to produce the composition.

Illustrative polyalphaolefin oligomers useful in the process of this disclosure include, for example, mPAO dimers, trimers, tetramers, higher oligomers, and the like.

In an embodiment, the mPAO dimer can be any dimer prepared from metallocene or other single-site catalyst with terminal double bond. The dimer can be from 1-decene, 1-octene, 1-dodecene, 1-hexene, 1-tetradecene, 1-octadecene or combination of alpha-olefins.

In another embodiment, an alkyl olefin such as 1-decene, 1-octene, 1-dodecene, 1-hexene, 1-tetradecene, 1-octadecene or combination of alpha-olefins can be used to react with an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol.

The olefin feed useful in the process of this disclosure can include a light olefinic byproduct fraction including dimers and light fractions from the metallocene-catalyzed PAO oligomerization process. These intermediate light fractions may be generally characterized as $C_{42}$ or lower olefinic distillate fractions that contain a mixture of highly reactive oligomers derived from the original alpha-olefin starting material.

The metallocene-derived intermediate useful as a feed material is produced by the oligomerization of an alpha-olefin feed using a metallocene oligomerization catalyst. The alpha olefin feeds used in this initial oligomerization step are typically alpha-olefin monomers of 4 to 24 carbon atoms, usually 6 to 20 and preferably 8 to 14 carbon atoms. Illustrative alpha olefin feeds include, for example, 1-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, and the like. The olefins with even carbon numbers are preferred as are the linear alpha-olefins, although it is possible to use branched-chain olefins containing an alkyl substituent at least two carbons away from the terminal double bond.

The initial oligomerization step using a metallocene catalyst can be carried out under the conditions appropriate to the selected alpha-olefin feed and metallocene catalyst. A preferred metallocene-catalyzed alpha-olefin oligomerization process is described in WO 2007/011973, which is incorporated herein by reference in its entirety and to which reference is made for details of feeds, metallocene catalysts, process conditions and characterizations of products.

The dimers useful as feeds in the process of this disclosure possess at least one carbon-carbon unsaturated double bond. The unsaturation is normally more or less centrally located at the junction of the two monomer units making up the dimer as a result of the non-isomerizing polymerization mechanism characteristic of metallocene processes. If the initial metallocene polymerization step uses a single 1-olefin feed to make an alpha-olefin homopolymer, the unsaturation will be centrally located but if two 1-olefin comonomers have been used to form a metallocene copolymer, the location of the double bond may be shifted off center in accordance with the chain lengths of the two comonomers used. In any event, this double bond is 1,2-substituted internal, vinylic or vinylidenic in character. The terminal vinylidene group is represented by the formula $R_aR_bC{=}CH_2$, referred to as vinyl when the formula is $R_aHC{=}CH_2$. The amount of unsaturation can be quantitatively measured by bromine number measurement according to ASTM D1159 or equivalent method, or according to proton or carbon-13 NMR. Proton NMR spectroscopic analysis can also differentiate and quantify the types of olefinic unsaturation.

Illustrative aliphatic polythiols, aromatic polythiols, cycloaliphatic polythiols, ester or acid containing thiols, and ester or acid containing polythiols useful in the process of this disclosure include, for example, 1,2-ethanedithiol, 3-mercaptopropionate, pentaerythritoltetrakis(3 mercaptopropionate), trimethylopropanetris(3-mercaptopropionate), and the like. The thiols can be primary or secondary, linear or branched thiols with alkyl carbon chain length of $C_6$-$C_{20}$ carbons. Higher thiols in the range $C_6$-$C_{18}$ are of particular industrial significance. This disclosure encompasses the whole group of primary and secondary, branched and unbranched, even- and odd-numbered thiols.

Illustrative aliphatic polythiols e.g., dithiols) useful in the process of this disclosure include, for example, 1,2-ethanedithiol, 1,11-undecanedithiol, 1,16-hexadecanedithiol, 1,3-propanedithiol, 1,4-butanedithiol, 1,5-pentanedithiol, 1,6-hexanethiol, 1,8-octanedithiol, 1,9-nonartedithiol, hexa(ethylene glycol)dithiol, tetra(ethylene glycol)dithiol, cyclohexanethiol, 2,4,4-trimethyl-2-pentanethiol, and the like, or a combination of those. One can also use functional thio-alkanes to react with mPAO dimer. Examples of functional thio-alkane include mercaptoethoxy ethanol ($HO—CH_2—CH_2—O—CH_2—CH_2—SH$), ethanethio, 2-ethoxy-($CH_3—CH_2—O—CH_2—CH_2—SH$), 1-mercapto-4,7,10-trioxaundecane ($HS—CH_2—CH_2—O—CH_2—CH_2—O—CH_2—CH_2—O—CH_3$), 2-(2-methoxyethoxy)ethanethiol, 2-(trimethylsilyl)ethanethiol, 2,2,2-trifluoroethanethiol, 5-mercapto-4H-[1,2,4]triazol-3-ol, thioglycolic acid, 2-mercaptoethanol, cysteamine, thiolactic acid, methylthioglycolate, 2-methoxyethanethiol, 2-mercaptoethyl ether, methylthioglycolate, 2-propene-1-thiol, 3-chloro-1-propanethiol, L-cysteine, 1-mercapto-2-propanol, 3-mercapto-1-propanol, 4-mercaptobutyric acid, 2-butanethiol, 2-(2-methoxyethoxy)ethanethiol, 3-mercapto-3-methyl-1-butyl-1-formate, 3-mercaptobutylacetate, 3-mercapto-1-hexanol, 6-mercapto-1-hexanol, 2-(butylamino) ethanethiol, 2-ethylhexyl thioglycolate, 3-mercaptohexyl butyrate, 3-mercaptopropionic acid, 8-mercaptooctanoic acid, 8-mercapto-1-octanol, 11-mercaptoundecanoic acid, 12-mercaptoundecanoic acid, 16-mercaptoundecanoic acid, trimethylpropane tris(3-mercaptopropionate), 3-mercaptohexylhexaanote, 2-ethylhexanethiol, O-[2-(3-mercaptopropionylamino)ethyl]-O'-methylpolyethylene glycol, O-(2-carboxyethyl)-O'-(2-mercaptoethyl)heptaethylene glycol, O-(2-mercaptoethyl)-O'-methyl-hexa(ethylene glycol), Mn=350, poly(ethylene glycol) methyl ether thiol, Mn=1000, poly(ethylene glycol)2-mercaptoethylether acetic acid, Mn=500.

Illustrative aromatic polythiols (e.g., dithiols) useful in the process of this disclosure include, for example, benzene-4,2-dithiol, benzene-1,3-dithiol, toluene-3,4-dithiol, biphenyl-4,4'-dithiol, 1,3-propanethiol, 2,3-dimercapto-1-propanol, 1,4-butanedithiol, 2,2'-thiodiethanethiol, 1,2-ethanedithiol, 1,4-butanedithiol, 1,5-pentanedithiol, 1,6-hexanedithiol, 1,11-undecanedithiol, 1,16-hexadecanedithiol, 1,9-nonanedithiol, 1,4-dithioerythritol, 2,2'-thiodiethanethiol, 2,3-butanedithiol, hexa(ethylene glycol)dithiol, tetra(ethylene glycol) dithiol, 2,2'-[ethylenedioxy]diethanethiol, 2-mercaptoethylether, poly(ethylene glycol)dithiol, and the like, or a combination of those.

Illustrative cycloaliphatic polythiols (e.g., dithiols) useful in the process of this disclosure include, for example, 1,4-cyclohexanedithiol, 1,2-cyclohexanedithiol, and the like or a combination of those.

Illustrative ester or acid containing thiols useful in the process of this disclosure include, for example, 3-mercaptopropionate, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid, thiosalicylic acid, and the like, or combination of those. Illustrative ester or acid containing polythiols (e.g., dithiols) useful in the process of this disclosure include, for example, pentaerythritoltetrakis(3-mercaptopropionate), trimethylopropanetris(3-mercaptopropionate), trimethylopropanetris (2-mercaptoacetate), and the like, or a combination of those.

Other types of thiols useful in the process of this disclosure include glycol ether thiols. For example, one can be use glycol ethers like di(ethylene glycol)monohexyl ether thiol, tri(ethylene glycol)monomethyl ether thiol, tri(propylene glycol)monomethyl ether thiol, tri(ethylene glycol)monoethyl ether thiol, tri(ethylene glycol)monobutyl ether thiol, di(ethylene glycol)monoethyl ether thiol, di(ethylene glycol) monobutyl ether thiol, tri(propylene glycol)monopropyl ether thiol, tri(propylene glycol)monobutyl ether thiol, poly (ethylene glycol) dodecyl ether thiol, ethylene glycol mono-2-ethylhexyl ether thiol, and the like.

Illustrative catalysts that optionally can be used in the process of this disclosure include, for example, free-radical initiators for olefin-thiol reactions, and the like. Other suitable catalysts include, for example, free-radical initiators that can be used for olefin-thiol reactions. The free radical initiators are well known to those skilled in the art. Illustrative initiators include, but are not limited to, organic peroxides, such as alkyl peroxides, dialkyl peroxides, aroyl peroxides and peroxy esters, and azo compounds. Preferred alkyl hydroperoxides include tertiary-butyl hydroperoxide, tertiary-octyl hydroperoxide and cumene hydroperoxide; preferred dialkyl peroxides include ditertiary-butyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane and di-cumyl peroxide; preferred aroyl peroxides include benzoyl peroxide; preferred peroxy esters include tertiary-butyl peroxypivalate, t-butylperoxy-2-ethylhexanoate (Trigonox 21®) and tertiary-butyl-perbenzoate; and preferred azo compounds include azo-bis-isobutyronitrile. Free radical initiators with an appropriate half-life at reaction temperatures ranging from 50° C. to 300° C. can be used. Of these, t-butyl peroxypivalate, t-butylperoxy-2-ethylhexanoate (Trigonox 21®) and t-butyl peroxide are most preferred. The catalyst can be used in conventional amounts needed to catalyze the reaction of the polyalphaolefin oligomer or alpha olefin and the end-functionalized alkane.

Suitable olefin-thiol reaction acid catalysts that can be used include, for example, acidic catalysts that can be a Lewis acid. The Lewis acid catalysts useful for coupling reactions include metal and metalloid halides conventionally used as Friedel-Crafts catalysts. Suitable examples include $AlCl_3$, $BF_3$, $AlBr_3$, $TiCl_3$, and $TiCl_4$, either as such or with a protic promoter. Other examples include solid Lewis acid catalysts, such as synthetic or natural zeolites; acid clays; polymeric acidic resins; amorphous solid catalysts, such as silica-alumina; and heteropoly acids, such as the tungsten zirconates, tungsten molybdates, tungsten vanadates, phosphotungstates and molybdotungstovanadogermanates (e.g. $WO_x/ZrO_2$ and $WO_x/MoO_3$). Beside these catalysts, acidic ionic liquid can also be used as catalysts for coupling reactions. Among different catalysts polymeric acidic resins, such as Amberlyst 15, Amberlyst 36 are most preferred. Typically, the amount of acid catalyst used is 0.1 to 30 weight % and preferably 0.2 to 5 weight % based on total weight of the feed.

Reaction conditions for the reaction of the polyalphaolefin oligomer with the aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, such as temperature, pressure and contact time, may also vary greatly and any suitable combination of such conditions may be employed herein. The reaction temperature may range between 25° C. to 250° C., and preferably between 30° C. to 200° C., and more preferably between 60° C. to 150° C. Normally the reaction is carried out under ambient pressure and the contact time may vary from a matter of seconds or minutes to a few hours or greater. The reactants can be added to the reaction mixture or combined in any order. The stir time employed can range from 0.5 to 48 hours, preferably from 1 to 36 hours, and more preferably from 2 to 24 hours.

In an embodiment, the process of this disclosure involves selective coupling of mPAO (metallocene polyalphaolefin) 1-decene dimer with an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol to form decease trimer analogues with polar heteroatom that can render unique lube properties (i.e., low viscosity PAO like excellent bulk flow properties with built-in polarity). For example, vinylidene double bond terminated 1-octene dimer and 1,2-ethanedithiol can be reacted to give a synthetic base stock.

Examples of techniques that can be employed to characterize the compositions formed by the process described above include, but are not limited to, analytical gas chromatography, nuclear magnetic resonance, thermogravimetric analysis (TGA), inductively coupled plasma mass spectrometry, differential scanning calorimetry (DSC), volatility and viscosity measurements.

This disclosure provides lubricating oils useful as engine oils and in other applications characterized by excellent solvency and dispersancy characteristics. The lubricating oils are based on high quality base stocks including a major portion of a hydrocarbon base fluid such as a PAO or GTL with a secondary cobase stock component which is a heteroatom-containing, aliphatic, aromatic or cycloaliphatic hydrocarbon as described herein. The lubricating oil base stock can be any oil boiling in the lube oil boiling range, typically between 100 to 450° C. In the present specification and claims, the terms base oil(s) and base stock(s) are used interchangeably.

The viscosity-temperature relationship of a lubricating oil is one of the critical criteria which must be considered when selecting a lubricant for a particular application. Viscosity Index (VI) is an empirical, unitless number which indicates the rate of change in the viscosity of an oil within a given temperature range. Fluids exhibiting a relatively large change in viscosity with temperature are said to have a low viscosity index. A low VI oil, for example, will thin out at elevated temperatures faster than a high VI oil. Usually, the high VI oil is more desirable because it has higher viscosity at higher temperature, which translates into better or thicker lubrication film and better protection of the contacting machine elements.

In another aspect, as the oil operating temperature decreases, the viscosity of a high VI oil will not increase as much as the viscosity of a low VI oil. This is advantageous because the excessive high viscosity of the low VI oil will decrease the efficiency of the operating machine. Thus high VI (HVI) oil has performance advantages in both high and low temperature operation. VI is determined according to ASTM method D 2270-93 [1998]. VI is related to kinematic viscosities measured at 40° C. and 100° C. using ASTM Method D 445-01.

Lubricating Oil Base Stocks

A wide range of lubricating oils is known in the art. Lubricating oils that are useful in the present disclosure are both natural oils and synthetic oils. Natural and synthetic oils (or mixtures thereof) can be used unrefined, refined, or rerefined (the latter is also known as reclaimed or reprocessed oil). Unrefined oils are those obtained directly from a natural or synthetic source and used without added purification. These include shale oil obtained directly from retorting operations, petroleum oil obtained directly from primary distillation, and ester oil obtained directly from an esterification process. Refined oils are similar to the oils discussed for unrefined oils except refined oils are subjected to one or more purification steps to improve the at least one lubricating oil property. One skilled in the art is familiar with many purification processes. These processes include solvent extraction, secondary distillation, acid extraction, base extraction, filtration, and percolation. Rerefined oils are obtained by processes) analogous to refined oils but using an oil that has been previously used as a feed stock.

Groups I, II, III, IV and V are broad categories of base oil stocks developed and defined by the American Petroleum Institute (API Publication 1509; www.API.org) to create guidelines for lubricant base oils. Group I base stocks generally have a viscosity index of between 80 to 120 and contain greater than 0.03% sulfur and less than 90% saturates. Group II base stocks generally have a viscosity index of between 80 to 120, and contain less than or equal to 0.03% sulfur and greater than or equal to 90% saturates. Group III stock generally has a viscosity index greater than 120 and contains less than or equal to 0.03% sulfur and greater than 90% saturates. Group IV includes polyalphaolefins (PAO). Group V base stocks include base stocks not included in Groups I-IV. The table below summarizes properties of each of these five groups.

| | Base Oil Properties | | |
|---|---|---|---|
| | Saturates | Sulfur | Viscosity Index |
| Group I | <90 and/or | >0.03% and | ≥80 and <120 |
| Group II | ≥90 and | ≤0.03% and | ≥80 and <120 |
| Group III | ≥90 and | ≤0.03% and | ≥120 |
| Group IV | Includes polyalphaolefins (PAO) products | | |
| Group V | All other base oil stocks not included in Groups I, II, III or IV | | |

Natural oils include animal oils, vegetable oils (castor oil and lard oil, for example), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful in the present disclosure. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrorefined, or solvent extracted.

Group II and/or Group III hydroprocessed or hydrocracked base stocks, as well as synthetic oils such as polyalphaolefins, alkyl aromatics and synthetic esters, i.e. Group IV and Group V oils are also well known base stock oils.

Synthetic oils include hydrocarbon oil such as polymerized and interpolymerized olefins (polybutyl ones, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers, for example). Polyalphaolefin (PAO) oil base stocks, the Group IV API base stocks, are a commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from $C_8$, $C_{10}$, $C_{12}$, $C_{14}$ olefins or mixtures thereof may be utilized. See U.S. Pat. Nos. 4,956,122; 4,827,064; and 4,827,073, which are incorporated herein by reference in their entirety. Group IV oils, that is, the PAO base stocks have viscosity indices preferably greater than 130, more preferably greater than 135, still more preferably greater than 140.

Esters in a minor amount may be useful in the lubricating oils of this disclosure. Additive solvency and seal compatibility characteristics may be secured by the use of esters such as the esters of dibasic acids with monoalkanols and the polyol esters of monocarboxylic acids. Esters of the former type include, for example, the esters of dicarboxylic acids such as phthalic acid, succinic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acid, alkenyl malonic acid, etc., with a variety of alcohols such as butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, etc. Specific examples of these types of esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, etc.

Particularly useful synthetic esters are those which are obtained by reacting one or more polyhydric alcohols, preferably the hindered polyols such as the neopentyl polyols; e.g., neopentyl glycol, trimethylol ethane, 2-methyl-2-propyl-1,3-propanediol, trimethylol propane, pentaerythritol and dipentaerythritol with alkanoic acids containing at least 4 carbon atoms, preferably $C_5$ to $C_{30}$ acids such as saturated straight chain fatty acids including caprylic acid, capric acids, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, and behenic acid, or the corresponding branched chain fatty acids or unsaturated fatty acids such as oleic acid, or mixtures of any of these materials.

Esters should be used in a amount such that the improved wear and corrosion resistance provided by the lubricating oils of this disclosure are not adversely affected.

Non-conventional or unconventional base stocks and/or base oils include one or a mixture of base stock(s) and/or base oil(s) derived from: (1) one or more Gas-to-Liquids (GTL) materials, as well as (2) hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s) and/or base oils derived from synthetic wax, natural wax or waxy feeds, mineral and/or non-mineral oil waxy feed stocks such as gas oils, slack waxes (derived from the solvent dewaxing of natural oils, mineral oils or synthetic oils; e.g., Fischer-Tropsch feed stocks), natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, foots oil or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials recovered from coal liquefaction or shale oil, linear or branched hydrocarbyl compounds with carbon number of 20 or greater, preferably 30 or greater and mixtures of such base stocks and/or base oils.

GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. GTL base stocks and/or base oils are GTL materials of lubricating viscosity that are generally derived from hydrocarbons; for example, waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feed stocks. GTL base stock(s) and/or base oil(s) include oils boiling in the lube oil boiling range (1) separated/fractionated from synthesized GTL materials such as, for example, by distillation and subsequently subjected to a final wax processing step which involves either or both of a catalytic dewaxing process, or a solvent dewaxing process, to produce tube oils of reduced/low pour point; (2) synthesized wax isomerates, comprising, for example, hydrodewaxed or hydroisomerized cat and/or solvent dewaxed synthesized wax or waxy hydrocarbons; (3) hydrodewaxed or hydroisomerized cat and/or solvent dewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxing dewaxed F-T waxy hydrocarbons, or hydrodewaxed or hydroisomerized/followed by cat (or solvent) dewaxing dewaxed, F-T waxes, or mixtures thereof.

GTL base stock(s) and/or base oil(s) derived from GTL materials, especially, hydrodewaxed or hydroisomerized/followed by cat and/or solvent dewaxed wax or waxy feed, preferably F-T material derived base stock(s) and/or base oil(s), are characterized typically as having kinematic viscosities at 100° C. of from 2 $mm^2/s$ to 50 $mm^2/s$ (ASTM D445). They are further characterized typically as having pour points of −5° C. to −40° C. or lower (ASTM D97). They are also characterized typically as having viscosity indices of 80 to 140 or greater (ASTM D2270).

In addition, the GTL base stock(s) and/or base oils) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this materially especially suitable for the formulation of low SAP products.

The term GTL base stock and/or base oil and/or wax isomerate base stock and/or base oil is to be understood as embracing individual fractions of such materials of wide viscosity range as recovered in the production process, mixtures of two or more of such fractions, as well as mixtures of one or two or more low viscosity fractions with one, two or more higher viscosity fractions to produce a blend wherein the blend exhibits a target kinematic viscosity.

The GTL material, from which the GTL base stock(s) and/or base oil(s) is/are derived is preferably an F-T material (i.e., hydrocarbons, waxy hydrocarbons, wax).

Base oils for use in the formulated lubricating oils useful in the present disclosure are any of the variety of oils corresponding to API Group I, Group II, Group III, Group IV, Group V and Group VI oils and mixtures thereof, preferably API Group II, Group III, Group IV, Group V and Group VI oils and mixtures thereof, more preferably the Group III to Group VI base oils due to their exceptional volatility, stability, viscometric and cleanliness features. Minor quantities of Group I stock, such as the amount used to dilute additives for blending into formulated lube oil products, can be tolerated but should be kept to a minimum, i.e. amounts only associated with their use as diluent/carrier oil for additives used on an "as received" basis. Even in regard to the Group II stocks, it is preferred that the Group II stock be in the higher quality range associated with that stock, i.e. a Group II stock having a viscosity index in the range 100<VI<120.

In addition, the GTL base stock(s) and/or base oil(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stock(s) and/or base oil(s) and hydrodewaxed, or hydroisomerized/cat (and/or solvent) dewaxed base stock(s) and/or base oil(s) typically have very low sulfur and nitrogen content, generally containing less than 10 ppm, and more typically less than 5 ppm of each of these elements. The sulfur and nitrogen content of GTL, base stock(s) and/or base oil(s) obtained from F-T material, especially F-T wax, is essentially nil. In addition, the absence of phosphorous and aromatics make this material especially suitable for the formulation of low sulfur, sulfated ash, and phosphorus (low SAP) products.

The basestock component of the present lubricating oils will typically be from 50 to 99 weight percent of the total composition (all proportions and percentages set out in this specification are by weight unless the contrary is stated) and more usually in the range of 80 to 99 weight percent.

Cobase Stock Components

Heteroatom-containing, aliphatic, aromatic and cycloaliphatic hydrocarbon cobase stock components useful in this disclosure include, for example, compositions containing one or more compounds represented by the formula

$$(R_1)_a(X)(R_2)_b$$

wherein $R_1$ and $R_2$ are the same or different and are the residue of an alkyl group having from 4 to 40 carbon atoms, X is the residue of an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, a is a value from 1 to 6, and b is a value from 0 to 6. The composition has a viscosity ($Kv_{100}$) from 2 to 30 at 100° C., and a viscosity index (VI) from 100 to 200.

Illustrative heteroatom-containing, aliphatic, aromatic and cycloaliphatic hydrocarbon cobase stock components useful in the present disclosure include, for example, the product of a $C_{20}$ dimer (mPAO dimer) reacted with 1,2-ethanedithiol, and the like.

Methods for the production of heteroatom-containing, aliphatic, aromatic and cycloaliphatic hydrocarbon cobase stock components suitable for use in the present disclosure are described herein. For example, a polyalphaolefin oligomer or α-olefin ($C_4$-$C_{40}$) can be reacted with an aliphatic, aromatic or cycloaliphatic polythiol. The reaction is carried out optionally in the presence of a catalyst. The reaction is carried out under reaction conditions sufficient to produce the heteroatom-containing, aliphatic, aromatic or cycloaliphatic hydrocarbon cobase stork as more fully described hereinabove.

The heteroatom-containing, aliphatic, aromatic or cycloaliphatic hydrocarbon cobase stock component is preferably present in an amount sufficient for providing solubility and dispersancy of polar additives and/or sludge in the lubricating oil. The heteroatom-containing, aliphatic hydrocarbon cobase stock component is present in the lubricating oils of this disclosure in an amount from 1 to 50 weight percent, preferably from 5 to 30 weight percent, and more preferably from 10 to 20 weight percent.

Other Additives

The formulated lubricating oil useful in the present disclosure may additionally contain one or more of the other commonly used lubricating oil performance additives including but not limited to dispersants, other detergents, corrosion inhibitors, rust inhibitors, metal deactivators, other anti-wear agents and/or extreme pressure additives, anti-seizure agents, wax modifiers, viscosity index improvers, viscosity modifiers, fluid-loss additives, seal compatibility agents, other friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, defoamants, demulsifiers, emulsifiers, densifiers, wetting agents, gelling agents, tackiness agents, colorants, and others. For a review of many commonly used additives, see Klamann in Lubricants and Related Products, Verlag Chemie, Deerfield Beach, Fla.; ISBN 0-89573-177-0. Reference is also made to "Lubricant Additives Chemistry and Applications" edited by Leslie R. Rudnick, Marcel Dekker, Inc. New York, 2003 ISBN: 0-8247-0857-1.

The types and quantities of performance additives used in combination with the instant disclosure in lubricant compositions are not limited by the examples shown herein as illustrations.

Viscosity Improvers

Viscosity improvers (also known as Viscosity Index modifiers, and VI improvers) increase the viscosity of the oil composition at elevated temperatures which increases film thickness, while having limited effect on viscosity at low temperatures.

Suitable viscosity improvers include high molecular weight hydrocarbons, polyesters and viscosity index improver dispersants that function as both a viscosity index improver and a dispersant. Typical molecular weights of these polymers are between 10,000 to 1,000,000, more typically 20,000 to 500,000, and even more typically between 50,000 and 200,000.

Examples of suitable viscosity improvers are polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. Polyisobutylene is a commonly used viscosity index improver. Another suitable viscosity index improver is polymethacrylate (copolymers of various chain length alkyl methacrylates, for example), some formulations of which also serve as pour point depressants. Other suitable viscosity index improvers include copolymers of ethylene and propylene, hydrogenated block copolymers of styrene and isoprene, and polyacrylates (copolymers of various chain length acrylates, for example). Specific examples include styrene-isoprene or styrene-butadiene based polymers of 50,000 to 200,000 molecular weight.

The amount of viscosity modifier may range from zero to 8 wt %, preferably zero to 4 wt %, more preferably zero to 2 wt % based on active ingredient and depending on the specific viscosity modifier used.

Antioxidants

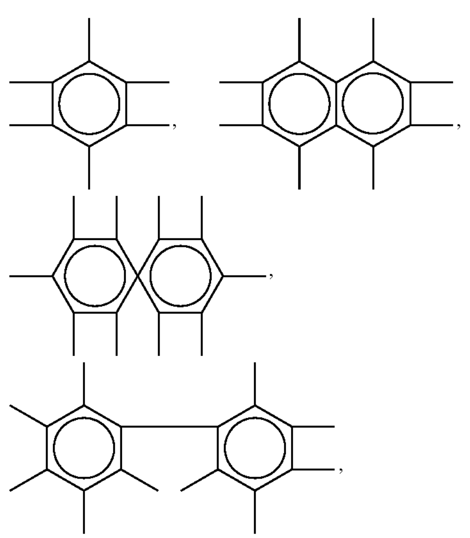
Typical antioxidant include phenolic antioxidants, aminic antioxidants and oil-soluble copper complexes.

The phenolic antioxidants include sulfurized and non-sulfurized phenolic antioxidants. The terms "phenolic type" or "phenolic antioxidant" used herein includes compounds having one or more than one hydroxyl group bound to an aromatic ring which may itself be mononuclear, e.g., benzyl, or poly-nuclear, e.g., naphthyl and spiro aromatic compounds. Thus "phenol type" includes phenol per se, catechol, resorcinol, hydroquinone, naphthol, etc., as well as alkyl or alkenyl and sulfurized alkyl or alkenyl derivatives thereof, and bisphenol type compounds including such bi-phenol compounds linked by alkylene bridges sulfuric bridges or oxygen bridges. Alkyl phenols include mono- and poly-alkyl or alkenyl phenols, the alkyl or alkenyl group containing from 3-100 carbons, preferably 4 to 50 carbons and sulfurized derivatives thereof, the number of alkyl or alkenyl groups present in the aromatic ring ranging from 1 to up to the available unsatisfied valences of the aromatic ring remaining after counting the number of hydroxyl groups bound to the aromatic ring.

Generally, therefore, the phenolic anti-oxidant may be represented by the general formula:

$$(R)_x\text{—Ar—}(OH)_y$$

where Ar is selected from the group consisting of:



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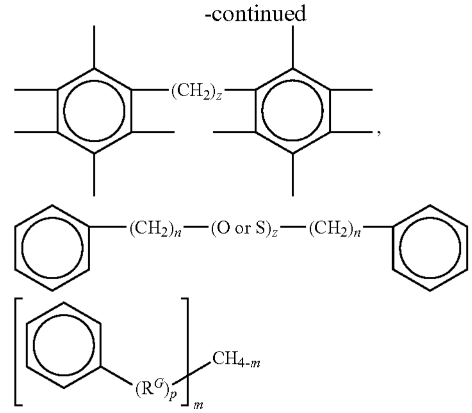
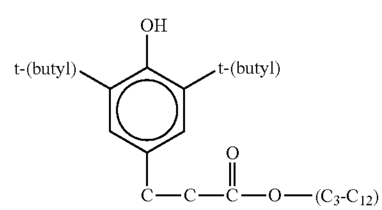



wherein R is a $C_3$-$C_{100}$ alkyl or alkenyl group, a sulfur substituted alkyl or alkenyl group, preferably a $C_4$-$C_{50}$, alkyl or alkenyl group or sulfur substituted alkyl or alkenyl group, more preferably $C_3$-$C_{100}$ alkyl or sulfur substituted alkyl group, most preferably a $C_4$-$C_{50}$ alkyl group, $R^G$ is a $C_1$-$C_{100}$ alkylene or sulfur substituted alkylene group, preferably a $C_2$-$C_{50}$ alkylene or sulfur substituted alkylene group, more preferably a $C_2$-$C_2$ alkylene or sulfur substituted alkylene group, y is at least 1 to up to the available valences of Ar, x ranges from 0 to up to the available valances of Ar-y, z ranges from 1 to 10, n ranges from 0 to 20, and m is 0 to 4 and p is 0 or 1, preferably y ranges from 1 to 3, x ranges from 0 to 3, z ranges from 1 to 4 and n ranges from 0 to 5, and p is 0.

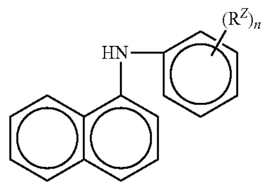
Preferred phenolic antioxidant compounds are the hindered phenolics and phenolic esters which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Typical phenolic anti-oxidants include the hindered phenols substituted with $C_1$+ alkyl groups and the alkylene coupled derivatives of these hindered phenols. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; 2-methyl-6-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4 methyl phenol; 2,6-di-t-butyl-4-ethyl phenol; and 2,6-di-t-butyl 4 alkoxy phenol; and




Phenolic type antioxidants are well known in the lubricating industry and commercial examples such as Ethanox® 4710, Irganox® 1076, Irganox® L1035, Irganox® 1010, Irganox® L109, Irganox® L118, Irganox® L 135 and the like are familiar to those skilled in the art. The above is presented only by way of exemplification, not limitation on the type of phenolic antioxidants which can be used.

The phenolic antioxidant can be employed in an amount in the range of 0.1 to 3 wt %, preferably 1 to 3 wt %, more preferably 1.5 to 3 wt % on an active ingredient basis.

Aromatic amine antioxidants include phenyl-α-naphthyl amine which is described by the following molecular structure:



wherein $R^z$ is hydrogen or a $C_1$ to $C_{14}$ linear or $C_3$ to $C_{14}$ branched alkyl group, preferably $C_1$ to $C_{10}$ linear or $C_3$ to $C_{10}$ branched alkyl group, more preferably linear or branched $C_6$ to $C_8$ and n is an integer ranging from 1 to 5 preferably 1. A particular example is Irganox L06.

Other aromatic amine antioxidants include other alkylated and non-alkylated aromatic amines such as aromatic monoamines of the formula $R^8R^9R^{10}N$ where $R^8$ is an aliphatic, aromatic or substituted aromatic group, $R^9$ is an aromatic or a substituted aromatic group, and $R^{10}$ is H, alkyl, aryl or $R^{11}S(O)_xR^{12}$ where $R^{11}$ is an alkylene, alkenylene, or aralkylene group, $R^{12}$ is a higher alkyl group, or an alkenyl, aryl, or alkaryl group, and x is 0, 1 or 2. The aliphatic group $R^8$ may contain from 1 to 20 carbon atoms, and preferably contains from 6 to 12 carbon atoms. The aliphatic group is a saturated aliphatic group. Preferably, both $R^8$ and $R^9$ are aromatic or substituted aromatic groups, and the aromatic group may be a fused ring aromatic group such as naphthyl. Aromatic groups $R^8$ and $R^9$ may be joined together with other groups such as S.

Typical aromatic amines antioxidants have alkyl substituent groups of at least 6 carbon atoms. Examples of aliphatic groups include hexyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than 14 carbon atoms. The general types of such other additional amine antioxidants which may be present include diphenylamines, phenothiazines, imidodibenzyls and diphenyl phenyl ene diamines. Mixtures of two or more of such other additional aromatic amities may also be present. Polymeric amine antioxidants can also be used.

Another class of antioxidant used in lubricating oil compositions and which may also be present are oil-soluble copper compounds. Any oil-soluble suitable copper compound may be blended into the lubricating oil. Examples of suitable copper antioxidants include copper dihydrocarbyl thio- or dithio-phosphates and copper salts of carboxylic acid (naturally occurring or synthetic). Other suitable copper salts include copper dithiocarbamates, sulphonates, phenates, and acetylacetonates. Basic, neutral, or acidic copper Cu(I) and or Cu(II) salts derived from alkenyl succinic acids or anhydrides are know to be particularly useful.

Such antioxidants may be used individually or as mixtures of one or more types of antioxidants, the total amount employed being an amount of 0.50 to 5 wt %, preferably 0.75 to 3 wt % (on an as-received basis).

Detergents

In addition to the alkali or alkaline earth metal salicylate detergent which is an essential component in the present disclosure, other detergents may also be present. While such other detergents can be present, it is preferred that the amount employed be such as to not interfere with the synergistic effect attributable to the presence of the salicylate. Therefore, most preferably such other detergents are not employed.

If such additional detergents are present, they can include alkali and alkaline earth metal phenates, sulfonates, carboxylates, phosphonates and mixtures thereof. These supplemental detergents can have total base number (TBN) ranging from neutral to highly overbased, i.e. TBN of 0 to over 500, preferably 2 to 400, more preferably 5 to 300, and they can be present either individually or in combination with each other in an amount in the range of from 0 to 10 wt %, preferably 0.5 to 5 wt % (active ingredient) based on the total weight of the formulated lubricating oil. As previously stated, however, it is preferred that such other detergent not be present in the formulation.

Such additional other detergents include by way of example and not limitation calcium phenates, calcium sulfonates, magnesium phenates, magnesium sulfonates and other related components (including borated detergents).

Dispersants

During engine operation, oil-insoluble oxidation byproducts are produced. Dispersants help keep these byproducts in solution, thus diminishing their deposition on metal surfaces. Dispersants may be ashless or ash-forming in nature. Preferably, the dispersant is ashless. So called ashless dispersants are organic materials that form substantially no ash upon combustion. For example, non-metal-containing or borated metal-free dispersants are considered ashless. In contrast, metal-containing detergents discussed above form ash upon combustion.

Suitable dispersants typically contain a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group typically contains at least one element of nitrogen, oxygen, or phosphorus. Typical hydrocarbon chains contain 50 to 400 carbon atoms.

A particularly useful class of dispersants are the alkenylsuccinic derivatives, typically produced by the reaction of a long chain substituted alkenyl succinic compound, usually a substituted succinic anhydride, with a polyhydroxy or polyamino compound. The long chain group constituting the oleophilic portion of the molecule which confers solubility in the oil, is normally a polyisobutylene group. Many examples of this type of dispersant are well known commercially and in the literature. Exemplary patents describing such dispersants are U.S. Pat. Nos. 3,172,892; 3,219,666; 3,316,177 and 4,234,435. Other types of dispersants are described in U.S. Pat. Nos. 3,036,003; and 5,705,458.

Hydrocarbyl-substituted succinic acid compounds are popular dispersants. In particular, succinimide, succinate esters, or succinate ester amides prepared by the reaction of a hydrocarbon-substituted succinic acid compound preferably having at least 50 carbon atoms in the hydrocarbon substituent, with at least one equivalent of an alkylene amine are particularly useful.

Succinimides are formed by the condensation reaction between alkenyl succinic anhydrides and amines. Molar ratios can vary depending on the amine or polyamine. For example, the molar ratio of alkenyl succinic anhydride to TEPA can vary from 1:1 to 5:1.

Succinate esters are formed by the condensation reaction between alkenyl succinic anhydrides and alcohols or polyols. Molar ratios can vary depending on the alcohol or polyol used. For example, the condensation product of an alkenyl succinic anhydride and pentaerythritol is a useful dispersant.

Succinate ester amides are formed by condensation reaction between alkenyl succinic anhydrides and alkanol amines. For example, suitable alkanol amines include ethoxylated polyalkylpolyamines, propoxylated polyalkylpolyamines and polyalkenylpolyamines such as polyethylene polyamines. One example is propoxylated hexamethylenediamine.

The molecular weight of the alkenyl succinic anhydrides will typically range between 800 and 2,500. The above products can be post-reacted with various reagents such as sulfur, oxygen, formaldehyde, carboxylic acids such as oleic acid, and boron compounds such as borate esters or highly borated dispersants. The dispersants can be borated with from 0.1 to 5 moles of boron per mole of dispersant reaction product.

Mannich base dispersants are made from the reaction of alkylphenols, formaldehyde, and amines. Process aids and catalysts, such as oleic acid and sulfonic acids, can also be part of the reaction mixture. Molecular weights of the alkylphenols range from 800 to 2,500.

Typical high molecular weight aliphatic acid modified Mannich condensation products can be prepared from high molecular weight alkyl-substituted hydroxyaromatics or $HN(R)_2$ group-containing reactants.

Examples of high molecular weight alkyl-substituted hydroxyaromatic compounds are polypropylphenol, polybutylphenol, and other polyalkylphenols. These polyalkylphenols can be obtained by the alkylation, in the presence of an alkylating catalyst, such as $BF_3$, of phenol with high molecular weight polypropylene, polybutylene, and other polyalkylene compounds to give alkyl substituents on the benzene ring of phenol having an average 600-100,000 molecular weight.

Examples of $HN(R)_2$ group-containing reactants are alkylene polyamines, principally polyethylene polyamines. Other representative organic compounds containing at least one $HN(R)_2$ group suitable for use in the preparation of Mannich condensation products are well known and include the mono- and di-amino alkanes and their substituted analogs, e.g., ethylamine and diethanol amine; aromatic diamines, e.g., phenylene diamine, diamino naphthalenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrrolidine, imidazole, imidazolidine, and piperidine; melamine and their substituted analogs.

Examples of alkylene polyamine reactants include ethylenediamine, diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, pentaethylene hexamine, hexaethylene heptaamine, heptaethylene octaamine, octaethylene nonaamine, nonaethylene decamine, and decaethylene undecamine and mixture of such amines having nitrogen contents corresponding to the alkylene polyamines, in the formula $H_2N—(Z—NH—)_nH$, mentioned before, Z is a divalent ethylene and n is 1 to 10 of the foregoing formula. Corresponding propylene polyamines such as propylene diamine and di-, tri-, tetra-, pentapropylene tri-, tetra-, penta- and hexaamines are also suitable reactants. The alkylene polyamines are usually obtained by the reaction of ammonia and dihalo alkanes, such as dichloro alkanes. Thus the alkylene polyamines obtained from the reaction of 2 to 11 moles of ammonia with 1 to 10 moles of dichloroalkanes having 2 to 6 carbon atoms and the chlorines on different carbons are suitable alkylene polyamine reactants.

Aldehyde reactants useful in the preparation of the high molecular products useful in this disclosure include the aliphatic aldehydes such as formaldehyde (also as paraformaldehyde and formalin), acetaldehyde and aldol (β-hydroxybutyraldehyde). Formaldehyde or a formaldehyde-yielding reactant is preferred.

Preferred dispersants include borated and non-borated succinimides, including those derivatives from mono-succinimides, leis-succinimides, and/or mixtures of mono- and bis-succinimides, wherein the hydrocarbyl succinimide is derived from a hydrocarbylene group such as polyisobutylene having a Mn of from 500 to 5000 or a mixture of such hydrocarbylene groups. Other preferred dispersants include succinic acid-esters and amides, alkylphenol-polyamine-coupled Mannich adducts, their capped derivatives, and other related components. Such additives may be used in an amount of 0.1 to 20 wt %, preferably 0.1 to 8 wt %, more preferably 1 to 6 wt % (on an as-received basis) based on the weight of the total lubricant.

Pour Point Depressants

Conventional pour point depressants (also known as lube oil flow improvers) may also be present. Pour point depressant may be added to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include alkylated naphthalenes polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers. Such additives may be used in amount of 0.0 to 0.5 wt %, preferably 0 to 0.3 wt %, more preferably 0.001 to 0.1 wt % on an as-received basis.

Corrosion Inhibitors/Metal Deactivators

Corrosion inhibitors are used to reduce the degradation of metallic parts that are in contact with the lubricating oil composition. Suitable corrosion inhibitors include aryl thiazines, alkyl substituted dimercapto thiodiazoles thiadiazoles and mixtures thereof. Such additives may be used in an amount of 0.01 to 0.5 wt %, preferably 0.01 to 1.5 wt %, more preferably 0.01 to 0.2 wt %, still more preferably 0.01 to 0.1 wt % (on an as-received basis) based on the total weight of the lubricating oil composition.

Seal Compatibility Additives

Seal compatibility agents help to swell elastomeric seals by causing a chemical reaction in the fluid or physical change in the elastomer. Suitable seal compatibility agents for lubricating oils include organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride and sulfolane-type seal swell agents such as Lubrizol 730-type seal swell additives. Such additives may be used in an amount of 0.01 to 3 wt %, preferably 0.01 to 2 wt %(0 on an as-received basis.

Anti-Foam Agents

Anti-foam agents may advantageously be added to lubricant compositions. These agents retard the formation of stable foams. Silicones and organic polymers are typical anti-foam agents. For example, polysiloxanes, such as silicon oil or polydimethyl siloxane, provide antifoam properties. Anti-foam agents are commercially available and may be used in conventional minor amounts along with other additives such as demulsifiers; usually the amount of these additives combined is less than 1 percent, preferably 0.001 to 0.5 wt %, more preferably 0.001 to 0.2 wt %, still more preferably 0.0001 to 0.15 wt % (on an as-received basis) based on the total weight of the lubricating oil composition.

Corrosion Inhibitors and Antirust Additives

Antirust additives (or corrosion inhibitors) are additives that protect lubricated metal surfaces against chemical attack by water or other contaminants. One type of antirust additive is a polar compound that wets the metal surface preferentially, protecting it with a film of oil. Another type of antirust additive absorbs water by incorporating it in a water-in-oil emulsion so that only the oil touches the surface. Yet another type of antirust additive chemically adheres to the metal to produce a non-reactive surface. Examples of suitable additives include zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids and amines. Such additives may be used in an amount of 0.01 to 5 wt %, preferably 0.01 to 1.5 wt % on an as-received basis.

In addition to the ZDDP anti-wear additives which are essential components of the present disclosure, other anti-wear additives can be present, including zinc dithiocarbamates, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, other organo molybdenum-nitrogen complexes, sulfurized olefins, etc.

The term "organo molybdenum-nitrogen complexes" embraces the organo molybdenum-nitrogen complexes described in U.S. Pat. No. 4,889,647. The complexes are reaction products of a fatty oil, diethanolamine and a molybdenum source. Specific chemical structures have not been assigned to the complexes. U.S. Pat. No. 4,889,647 reports an infrared spectrum for a typical reaction product of that disclosure; the spectrum identifies an ester carbonyl band at 1740 $cm^{-1}$ and an amide carbonyl band at 1620 $cm^{-1}$. The fatty oils are glyceryl esters of higher fatty acids containing at least 12 carbon atoms up to 22 carbon atoms or more. The molybdenum source is an oxygen-containing compound such as ammonium molybdates, molybdenum oxides and mixtures.

Other organo molybdenum complexes which can be used in the present disclosure are tri-nuclear molybdenum-sulfur compounds described in EP 1 040 115 and WO 99/31113 and the molybdenum complexes described in U.S. Pat. No. 4,978,464.

In the above detailed description, the specific embodiments of this disclosure have been described in connection with its preferred embodiments. However, to the extent that the above description is specific to a particular embodiment or a particular use of this disclosure, this is intended to be illustrative only and merely provides a concise description of the exemplary embodiments. Accordingly, the disclosure is not limited to the specific embodiments described above, but rather, the disclosure includes all alternatives, modifications, and equivalents falling within the true scope of the appended claims. Various modifications and variations of this disclosure will be obvious to a worker skilled in the art and it is to be understood that such modifications and variations are to be included within the purview of this application and the spirit and scope of the claims.

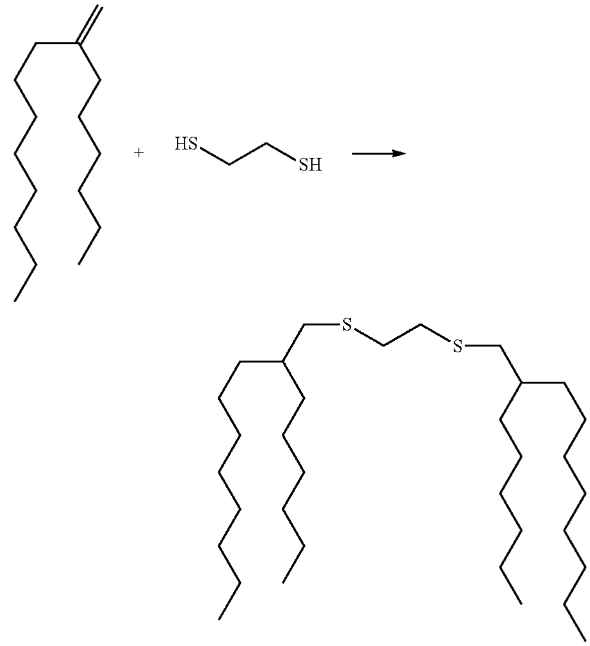
## EXAMPLES

### Example 1

### Reaction of Vinylidene Double Bond Terminated 1-Octene Dimer and 1,2-Ethanethiol

Charged 14.89 grams (0.0665 mole) $C_{16}$ dimer, 2.5 grams (0.0266 mole) 1,2-ethanedithiol and 1.09 grams (0.00665 mole) 2,2'-azobis(2-methylpropionitrile) (AIBN) into a 50 milliliter thick sealed glass reactor. After addition, the reaction mixture was stirred for 24 hours at 125° C. The reaction was stopped and cooled down to room temperature. The low boiling 1,2-ethanedithiol was removed by rotavapory and high boiling component $C_{16}$ dimer by air bath oven at 190-200° C. under vacuum for 1 hour. The final product was determined by IR, $^{1}H$ and $^{13}C$ NMR. Yields: 8.1 grams (56%). The reaction is illustrated below.

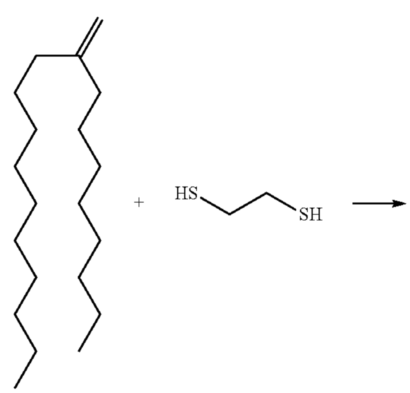
IR: ($cm^{-1}$) 2955, 2924, 2853, 1466, 1377, 1270, 1977, 722; $^{1}H$ NMR ($CDCl_3$): 2.72-2.61 (4H, d), 2.51 (4H, d), 1.52 (2H, d), 1.28 (48H, m), 0.88 (12H, t); $^{13}C$ NMR ($CDCl_3$): 38.0, 37.3, 33.7, 32.9, 31.9, 20.0, 29.6, 29.3, 22.7, 14.0.




### Example 2

### Reaction of Vinylidene Double Bond Terminated 1-Decene Dime and 1,2-ethanedithiol

Charged 7.5 grams (0.0266 mole) $C_{20}$ dimer, 1.0 grams (0.011 mole) 1,2-ethanedithiol and 0.0436 grams (0.00265 mol) 2,2'-azobis(2-methylpropionitrile) (AIBN) into a 25 milliliter thick scaled glass reactor. After addition, the reaction mixture was stirred for 20 hours at 125° C. The reaction was stopped and cooled down to room temperature. The low boiling 1,2-ethanedithiol was removed by rotavapory and high boiling component $C_{20}$ dimer by air bath oven at 190-200° C. under vacuum for 1 hour. The reaction is illustrated below. The final product was determined by IR, $^{1}H$ NMR. Yields: 6.0 grams (83%). IR: ($cm^{-1}$) 2955, 2923, 2853, 1466, 1377, 1197, 721; $^{1}H$ NMR ($CDCl_3$): 2.67 (4H, S), 2.51 (4H, d), 1.52 (2H, d), 1.28 (64H, m), 0.88 (12H, t).



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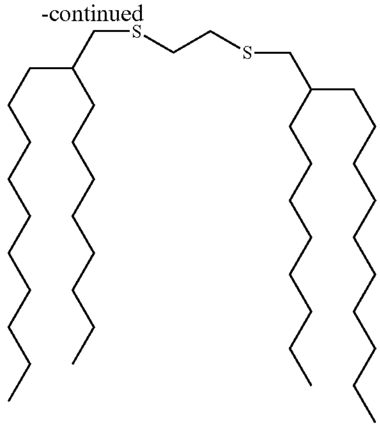



## Lube Properties of Base Stocks

The lube properties of the products of Examples 1 and 2 were evaluated and data are shown below along with PAO4 (1-decene trimer-tetramer mixture) and PAO3.4 (decene trimer). The kinematic viscosity (Kv) of the liquid product was measured using ASTM standards D-445 and reported at temperatures of 100° C. (Kv at 100° C.) or 40° C. (Kv at 40° C.). The viscosity index (VI) was measured according to ASTM standard D-2270 using the measured kinematic viscosities for each product. The lube properties of the products of Examples 1 and 2 were evaluated and the data are shown below along with PAO3.4 and PAO4.

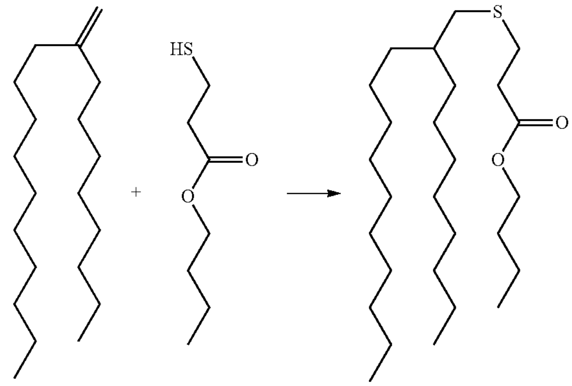
| Base stock# | Kinematic Viscosity at 100° C. ($Kv_{100}$) | Kinematic Viscosity at 40° C. ($Kv_{40}$) | Viscosity Index |
|---|---|---|---|
| Example 1 | 4.75 | 22.12 | 139 |
| Example 2 | 5.97 | 28.58 | 161 |
| PAO3.4 | 3.39 | 13.5 | 128 |
| PAO4 | 4.1 | 19 | 126 |

The products of Examples 1 and 2 have very good viscosity index. The product volatility was measured using thermogravimetric analysis (TGA).

### Example 3

### Reaction of Vinylidene Double Bond Terminated 1-Decene Dimer and 3-Mercaptopropionate

Charged 5 grams (0.0179 mole) $C_{20}$ dimer, 5.79 grams (0.0357 mole) 3-mercaptopropionate and 0.294 grams (0.00179 mol) 2,2'-azobis(2-methylpropionitrile) (AIBN) into a 50 milliliter thick sealed glass reactor. After addition, the reaction mixture was stirred for 20 hours at 120° C. The reaction was stopped and cooled down to room temperature. The low boiling 3-mercaptopropionate was removed by rotavapory and high boiling component $C_{20}$ dimer by air bath oven at 190-200° C. under vacuum for 1 hour. The proton NMR showing the complete conversion of vinylidene double bond and the formation of thioether linkage (—$CH_2$—S—$CH_2$—). The reaction is illustrated below. The final product was determined by IR, $^1$HNMR. Yields: 7.0 grams (89%) IR: ($cm^{-1}$) 2957, 2925, 2854, 1739, 1466, 1370, 1348, 1243, 1172, 1065, 722. $^1$H NMR ($CDCl_3$): 4.12 (2H, t), 2.75 (2h, t), 2.60 (2H, t) 2.49 (2H, d), 1.28-1.1.61 (38H, m), 0.88-0.93 (9H, m).




## Oxidation Performance of Base Stocks

Pressure Differential Scanning calorimetry (PDSC) is a useful screening tool for measuring oxidative stability. PDSC is used to determine oxidation under heating conditions. A heating experiment measures the temperature at which oxidation initiates under oxygen pressure. A DSC Model 2920 (TA instruments) with a pressure cell was used for the measurements. The cell is well calibrated for temperature (+/−0.3° C.) and heat flow (better than 1%) and checked for reproducibility daily with a quality control standard for temperature and heat response. The heating measurements were carried out at a heating rate of 10° C./min using pressure of 100 psi in air.

The heating-in-air data showed that oxidation of product of base stock of Example 3 occurs at 287.33° C. compared to mPAO3.4 for which the oxidation occurred at 204.83° C. Thus, there is a substantial improvement in oxidation stability of the heteroatom containing base stock. The product was also evaluated in TGA. The data suggest that the base stock of Example 3 has low volatility compare to PAO3.4.

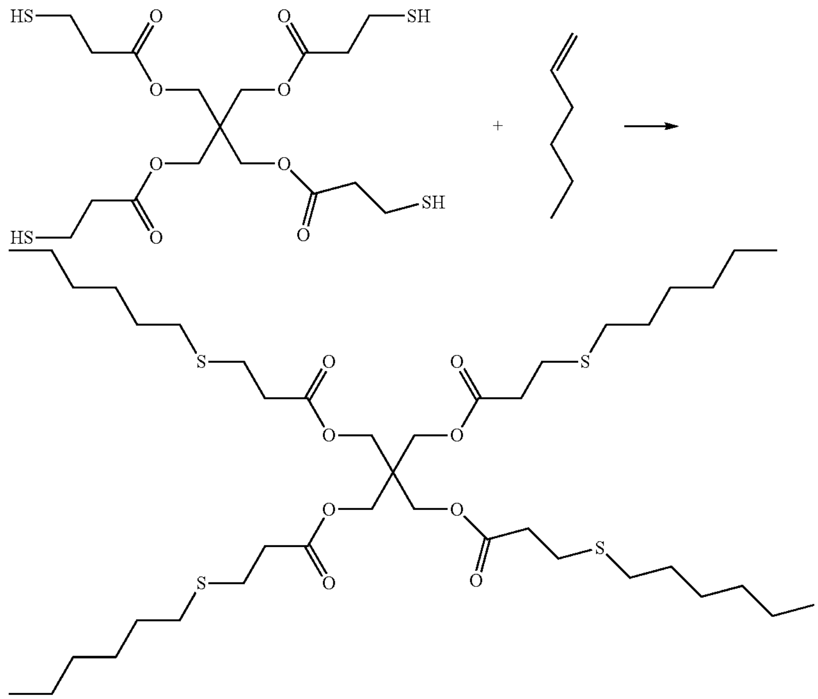
| Base Stock | Kinematic Viscosity at 100° C. | Viscosity Index | TGA (50 wt. loss) | DSC, oxi $T_{onset}$ |
|---|---|---|---|---|
| Example 3 | 3.23 | 149 | 280.58 | 287.33 |
| PAO3.4 | 3.4 | 128 | 263.1 | 204.83 |

Thus, the synthetic base stock of the Example 3 has lower viscosity than PAO03.4, higher viscosity index, lower volatility and higher oxidative stability. Moreover, this fluid is soluble in other base stocks including mPAO 150.

### Example 4

### Reaction of Pentaerythritoltetrakis(3-mercaptopropionate) with 1-Hexene

Charged 10 grams (0.0205 mole) pentaerythritoltetrakis(3-mercaptopropionate), 10.34 grams (0.1230 mole) 1-hexene and 0.336 grams (0.0021 mol) 2,2'-azobis(2-methylpropionitrile) (AIBN) in 50 milliliters toluene into a 250 milliliter thick sealed glass reactor. After addition, the reaction mixture was stirred for 20 hours at 100° C. The reaction was stopped and cooled down to room temperature. The low boiling 1-hexene and toluene was removed by rotavapory and high boiling component by air bath oven at 180° C. under vacuum for 1 hour. The proton NMR showing the formation of thioether linkage (—$CH_2$—S—$CH_2$—). The reaction is illustrated below. The final product was determined by IR, $^1$H NMR. Yields: 17 grams (100%). IR: ($cm^{-1}$): 2956, 2856, 1743, 1466, 1417, 1379, 1350, 1284, 1338, 1140, 1032, 727. $^1$H NMR ($CDCl_3$): 4.16 (8H, S), 2.75 (8H, m), 2.62 (8H, m), 2.52 (8H, m), 1.57 (8H, m), 1.37-1.29 (24H, m) 0.89 (12H, t).



The product was also evaluated in TGA. The data suggest that the base stock of Example 4 has better thermal stability than PAO 10. Both these fluids have same 100° C. viscosity.

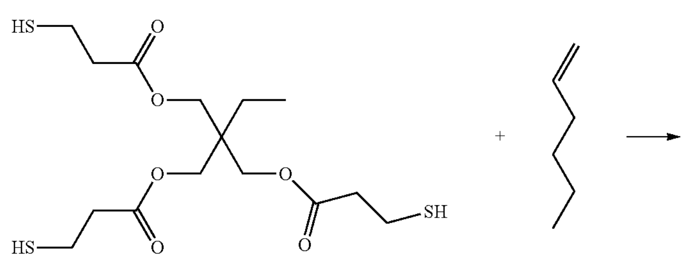
| Base Stock # | Kinematic Viscosity at 100° C. | TGA (50% wt. loss) |
|---|---|---|
| Example 4 | 10.4 | 377.06 |
| PAO 10 | 10 | 345.82 |

PDSC was used for measuring oxidative stability of the basestock. The heating-in-air data showed that oxidation of product of base stock of Example 4 occurs at 230° C. compared to PAO 6 for which the oxidation occurred at 197° C. Thus, there is a substantial improvement in oxidation stability of the heteroatom containing base stock.

Example 5

Reaction of Trimethylopropanetris(3-mercaptopropionate) with 1-Hexene

Charged 10 grams (0.0251 mole) trimethylopropanetris(3-mercaptopropionate), 12.67 grams (0.1505 mole) 1-hexene and 0.412 grams (0.0025 mole) 2,2'-azobis(2-methylpropionitrile) (AIBN) in 15 milliliters of toluene into a 250 milliliter thick sealed glass reactor. After addition, the reaction mixture was stirred for 48 hours at 100° C. The reaction was stopped and cooled down to room temperature. The low boiling toluene was removed by rotavapory and high boiling mPAO $C_{20}$ dimer by air bath oven at 200° C. under vacuum for 1 hour. The proton NMR showed the formation of thioether linkage (—$CH_2$—S—$CH_2$—). The reaction is illustrated below. The final product was determined by IR, $^1$H NMR. Yields: 16.3 grams (100%). IR: ($cm^{-1}$) 2956, 2927, 2857, 1743, 1465, 1419, 1380, 1350, 1284, 1239, 1141, 1055, 994, 785, 725. $^1$H NMR ($CDCl_3$): 4.06 (8H, S), 2.76 (8H, m), 2.61 (8H, m), 2.52 (8H, m), 1.57 (8H, m), 1.37-1.29 (16H, m) 0.89 (12H, t).



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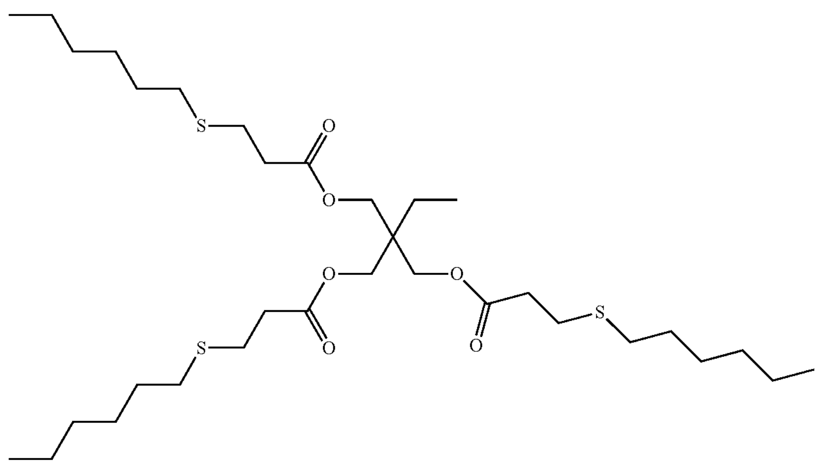



The product was also evaluated in TGA. The data suggest that the base stock of Example 5 has better thermal stability than PAO 4 and PAO 10.

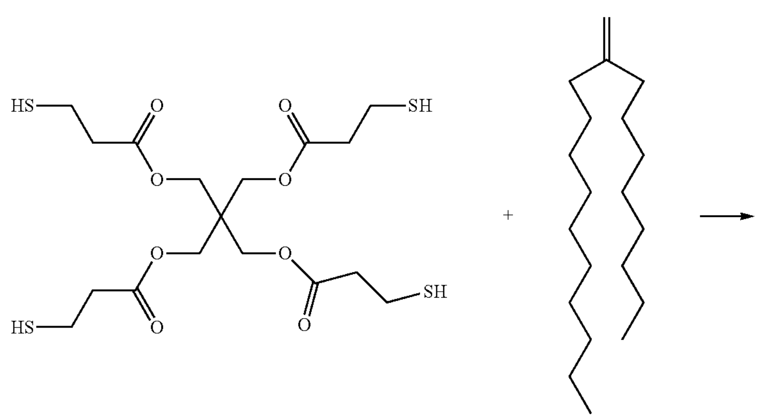
| Base Stock # | Kinematic Viscosity at 100° C. | Kinematic Viscosity at 40° C. | Viscosity Index (VI) | TGA (50% wt. loss) |
|---|---|---|---|---|
| Example 5 | 7.6 | 44.1 | 139.7 | 354.24 |
| PAO 4 | 4.1 | 19 | 126 | 266.82 |
| PAO 10 | 10 | 66 | 137 | 345.82 |

PDSC was used for measuring oxidative stability of the basestock. The heating-in-air data showed that oxidation of product of base stock of Example 5 occurs at 257.76° C. compared to PAO 6 for which the oxidation occurred at 197° C. Thus, there is a substantial improvement in oxidation stability of the heteroatom containing base stock.

## Example 6

### Reaction of Pentaerythritoltetrakis(3-mercaptopropionate) with mPAO Dimer

Charged 2.5 grams (0.0256 mole) pentaerythritoltetrakis (3-mercaptopropionate), 8.5 grams (0.02556 mole) mPAO dimer and 0.335 grams (0.00204 mole) 2,2'-azobis(2-methylpropionitrile) (AIBN) in 15 milliliters of toluene into a 250 ml thick sealed glass reactor. After addition, the reaction mixture was stirred for 48 hours at 120° C. The reaction was stopped and cooled down to room temperature. The low boiling 1-hexene and toluene was removed by rotavapory and high boiling component by air bath oven at 200° C. under vacuum for 1 hour. The proton NMR showed the formation of thioether linkage (—$CH_2$—S—$CH_2$—). The reaction is illustrated below. The final product was determined by IR, $^1$H NMR, Yields: 8 grams (97%). IR: ($cm^{-1}$): 2955, 2924, 2853, 1745, 1466, 1378, 1350, 1237, 1142, 1031, 721. $^1$H NMR ($CDCl_3$): $^1$H NMR ($CDCl_3$): 4.16 (8H, S), 2.74 (8H, m), 2.63 (8H, m), 2.49 (8H, m), 1.57 (4H, m), 1.26 (128H, m) 0.88 (24H, t).



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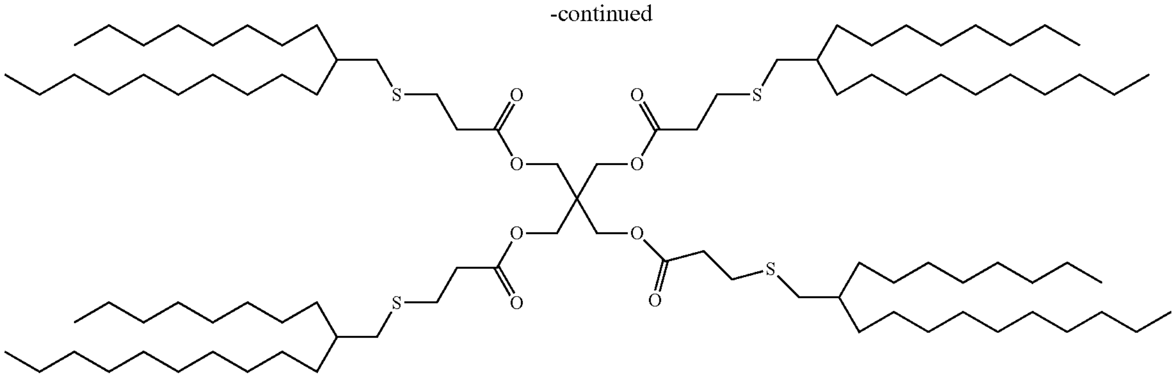



## Example 7

### Reaction of Trimethylopropanetris(3-mercaptopropionate) with mPAO Dimer

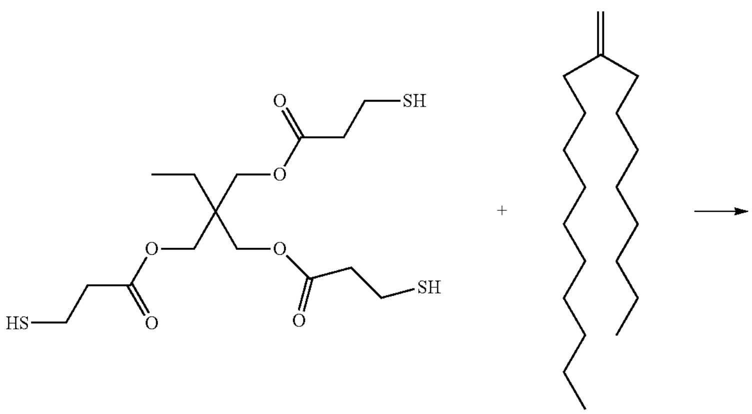
Charged 2.5 grams (0.0256 mole) trimethylopropanetris (3-mercaptopropionate), 8.8 grams (0.0313 mole) in PAO dimer and 0.301 grams (0.00184 mol) 2,2'-azobis(2-methyl-propionitrile) (AIBN) in 15 milliliters of toluene into 250 ml thick sealed glass reactor. After addition, the reaction mixture was stirred for 48 hours at 120° C. The reaction was stopped and cooled down to room temperature. The low boiling 1-hexene and toluene was removed by rotavapory and high boiling component by air bath oven at 200° C. under vacuum for 1 hour. The IR showed the formation of thioether linkage (—$CH_2$—S—$CH_2$—). The reaction is illustrated below. The final product was determined by IR. Yields: 7.6 grams (97%).

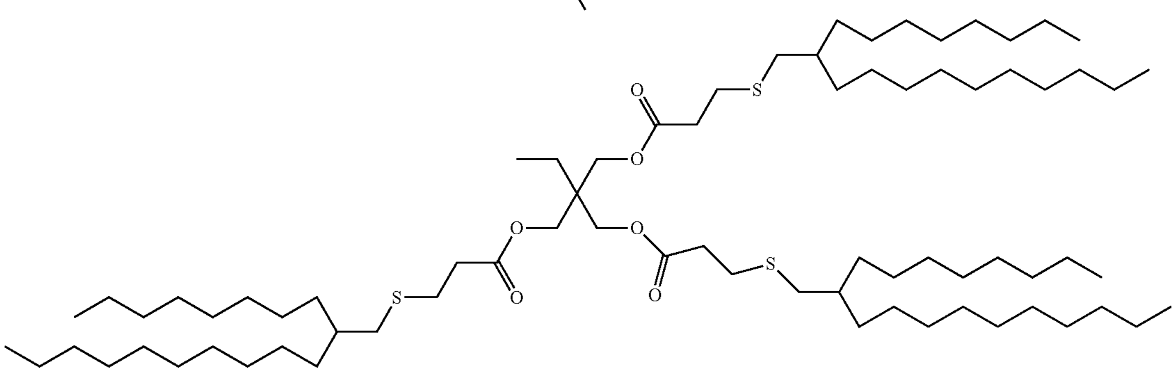
Lube Properties of Base Stocks of Examples 6 and 7

The kinematic viscosity (Kv) of the liquid product was measured using ASTM standards D-445 and reported at temperatures of 100° C. (Kv at 100° C.) or 40° C. (Kv at 40° C.). The viscosity index (VI) was measured according to ASTM standard D-2270 using the measured kinematic viscosities for each product. The viscometric properties of the base stock of Examples 6 and 7 are shown in the table below.

| Base Stock # | Kinematic Viscosity at 100° C. | Kinematic Viscosity at 40° C. | Viscosity Index (VI) |
|---|---|---|---|
| Example 6 | 16.3 | 127.21 | 136.2 |
| Example 7 | 8.9 | 49.95 | 158.6 |
| PAO 10 | 10 | 66 | 137 |

All these fluids are stable Group V base stocks.



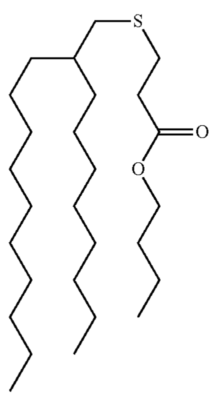



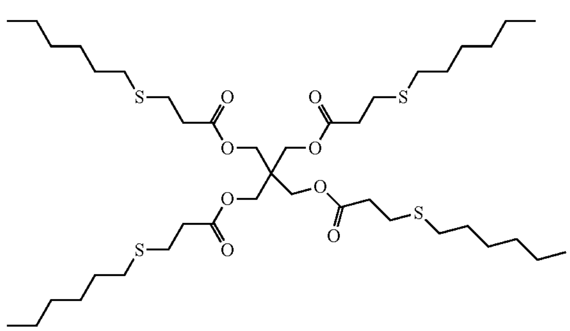
What is claimed is:

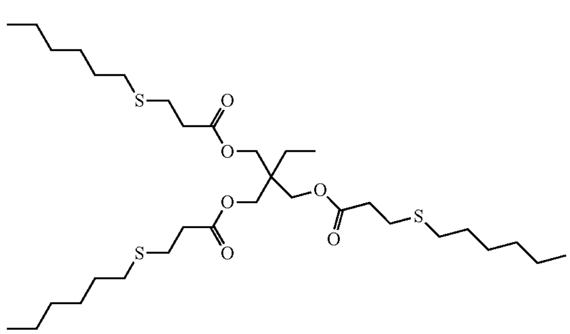
1. A composition comprising one or more compounds represented by the formula

$$(R_1)_a(X)(R_2)_b$$

wherein $R_1$ and $R_2$ are the same or different and are the residue of an alkyl group having from 4 to 40 carbon atoms, X is the residue of an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, a is a value from 1 to 6, and b is a value from 0 to 6; wherein said composition has a viscosity ($Kv_{100}$) from 2 to 30 at 100° C., and a viscosity index (VI) from 100 to 200, wherein the composition comprises a heteroatom-containing polyalphaolefin oligomer, or one or more compounds represented by the following formula:









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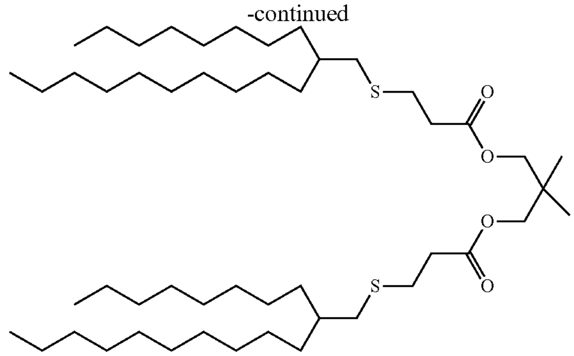
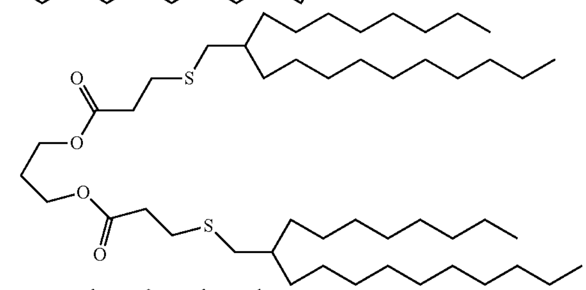
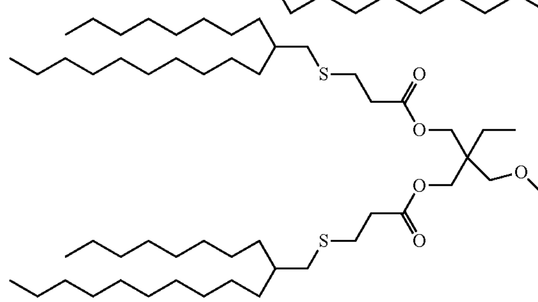
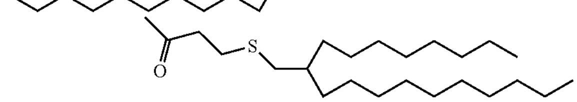






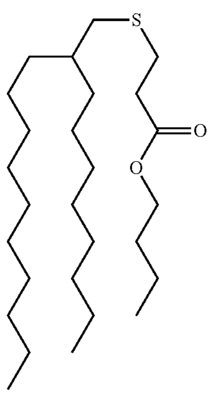


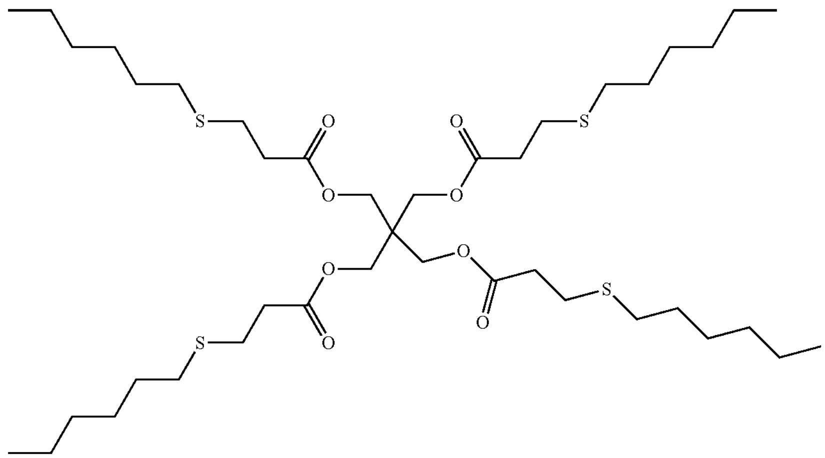
2. The composition of claim **1** wherein $R_1$ and $R_2$ are selected from the residue of a mPAO dimer ($C_6$-$C_{40}$), trimer ($C_6$-$C_{40}$), tetramer ($C_6$-$C_{40}$), pentamer ($C_6$-$C_{40}$), and hexamer ($C_6$-$C_{40}$), or α-olefin ($C_4$-$C_{40}$), X is selected from the residue of 1,2-ethanedithiol, 3-mercaptopropionate, pentaerythritoltetrakis(3-mercaptopropionate), and trimethylopropanetris(3-mercaptopropionate), a is a value from 1 to 4, and b is a value or 0 or 1.

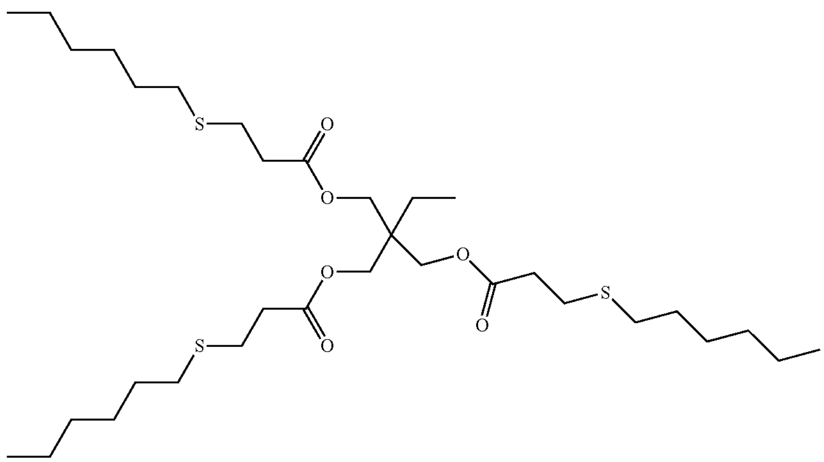
3. The composition of claim **1** having a Noack volatility of no greater than 20 percent.

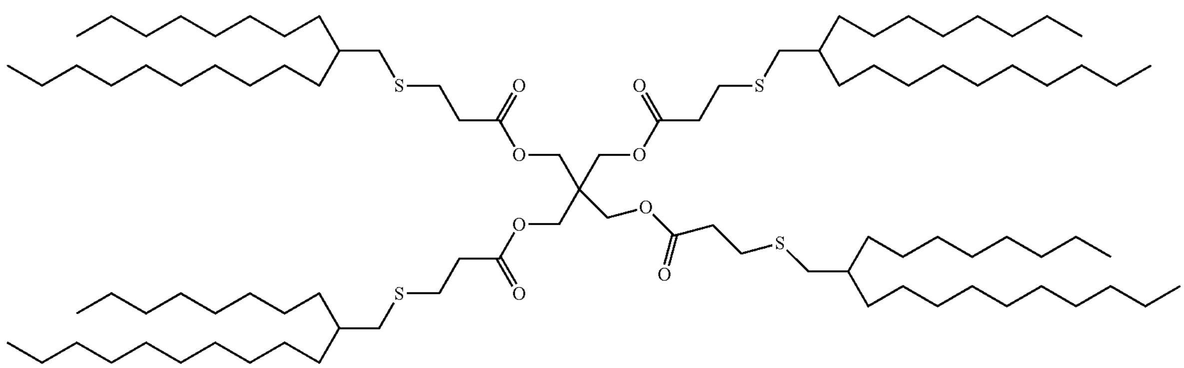
4. The composition of claim **1** wherein the heteroatom-containing polyalphaolefin oligomer is selected from a heteroatom-containing mPAO dimer, trimer, tetramer, pentamer, hexamer and higher oligomer.

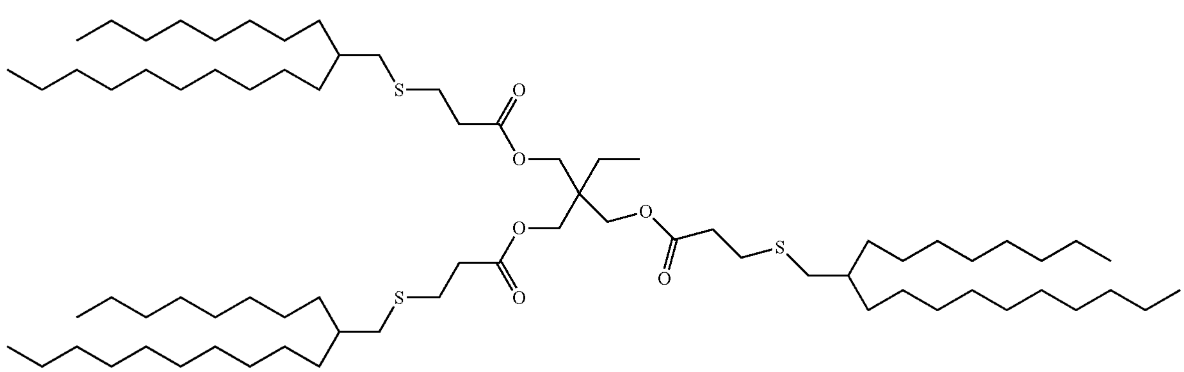
5. A composition comprising one or more heteroatom-containing hydrocarbon compounds, wherein said one or more heteroatom-containing hydrocarbon compounds are produced by a process comprising reacting a polyalphaolefin oligomer or α-olefin ($C_4$-$C_{40}$) with an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, optionally in the presence of a catalyst, under reaction conditions sufficient to produce said one or more heteroatom-containing hydrocarbon compounds, wherein the composition comprises a heteroatom-containing polyalphaolefin oligomer, or one or more compounds represented by the following formula:









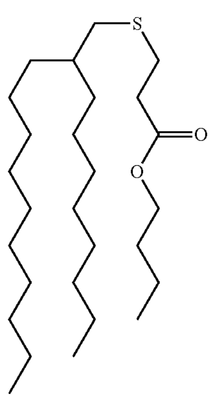


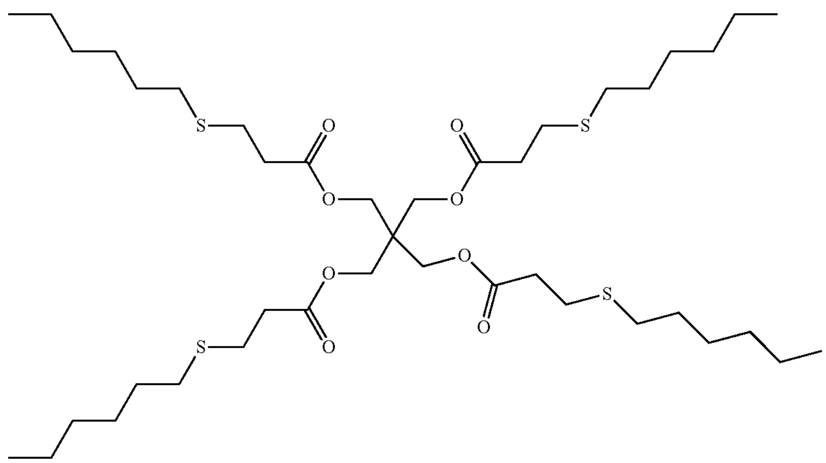
 

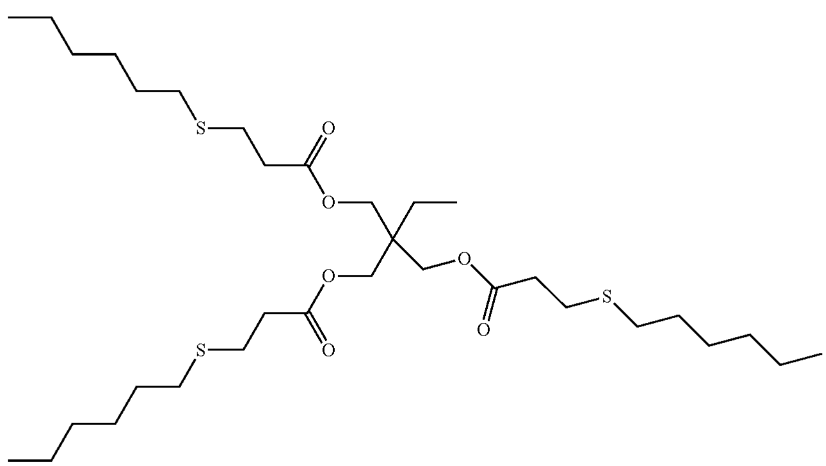
6. The composition of claim 5 wherein the process is carried out under reaction conditions sufficient to couple the polyalphaolefin oligomer or α-olefin ($C_4$-$C_{40}$) with the aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, to produce said heteroatom-containing hydrocarbon compound.

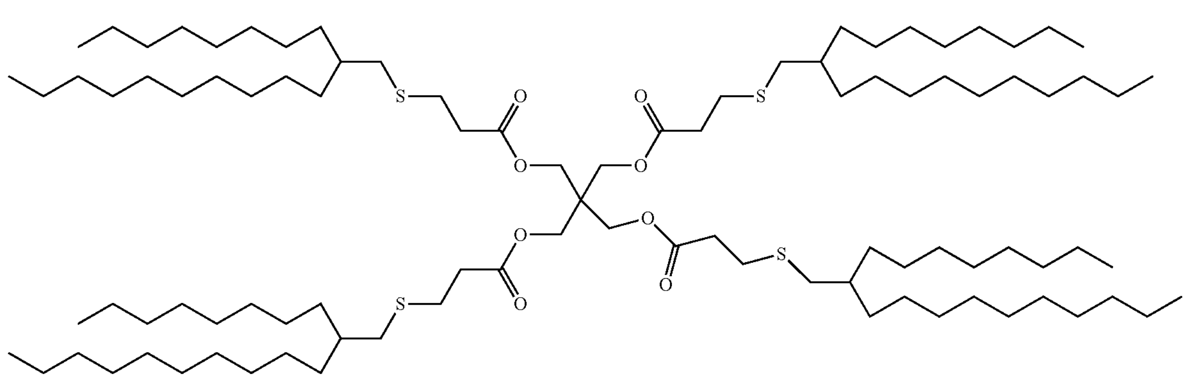
7. The composition of claim 5 having a viscosity ($Kv_{100}$) from 2 to 30 at 100° C., a viscosity index (VI) from 100 to 200, and a Noack volatility of no greater than 20 percent.

8. A process for producing a composition comprising one or more heteroatom-containing hydrocarbon compounds, said process comprising reacting a polyalphaolefin oligomer or α-olefin ($C_4$-$C_{40}$) with an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, optionally in the presence of a catalyst, under reaction conditions sufficient to produce said composition, wherein the composition comprises a heteroatom-containing polyalphaolefin oligomer, or one or more compounds represented by the following formula:









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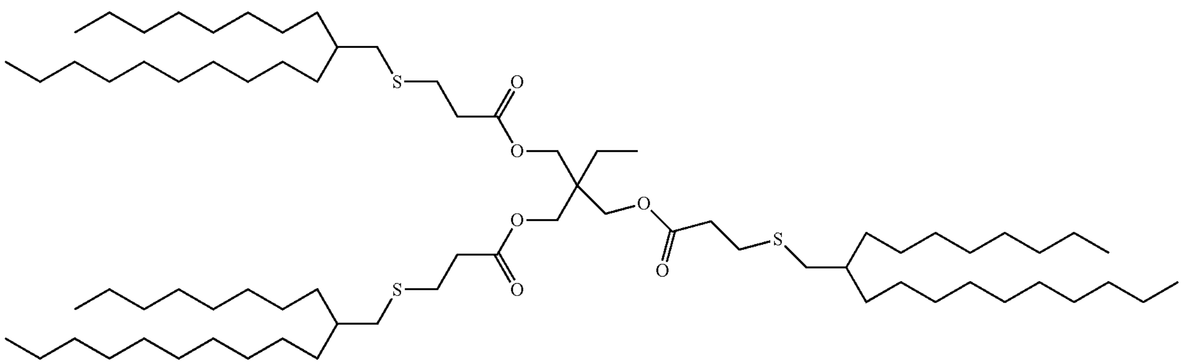


9. The process of claim 8 wherein the polyalphaolefin oligomer is selected from a mPAO dimer ($C_6$-$C_{40}$), trimer ($C_6$-$C_{40}$), tetramer ($C_6$-$C_{40}$), pentamer ($C_6$-$C_{40}$), and hexamer ($C_6$-$C_{40}$), and the aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol is selected from 1,2-ethanedithiol, 3-mercaptopropionate, pentaerythritoltetrakis (3-mercaptopropionate), and trimethylopropanetris(3-mercaptopropionate).

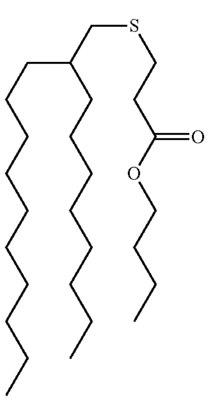
10. The process of claim 8 which is carried out under reaction conditions sufficient to couple the polyalphaolefin oligomer or α-olefin ($C_4$-$C_{40}$) with the aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, to produce said composition.

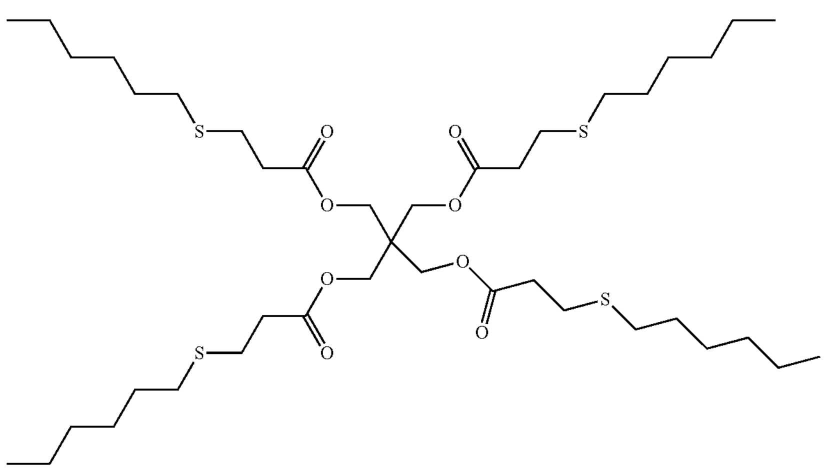
11. The process of claim 8 wherein the composition has a viscosity ($Kv_{100}$) from 2 to 30 at 100° C., a viscosity index (VI) from 100 to 200, and a Noack volatility of no greater than 20 percent.

12. A lubricating oil base stock comprising one or more compounds represented by the formula

$$(R_1)_a(X)(R_2)_b$$

wherein $R_1$ and $R_2$ are the same or different and are the residue of an alkyl group having from 4 to 40 carbon atoms, X is the residue of an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, a is a value from 1 to 6, and b is a value from 0 to 6; wherein said composition has a viscosity ($Kv_{100}$) from 2 to 30 at 100° C., a viscosity index (VI) from 100 to 200, and a Noack volatility of no greater than 20 percent, wherein the composition comprises a heteroatom-containing polyalphaolefin oligomer, or one or more compounds represented by the following formula:





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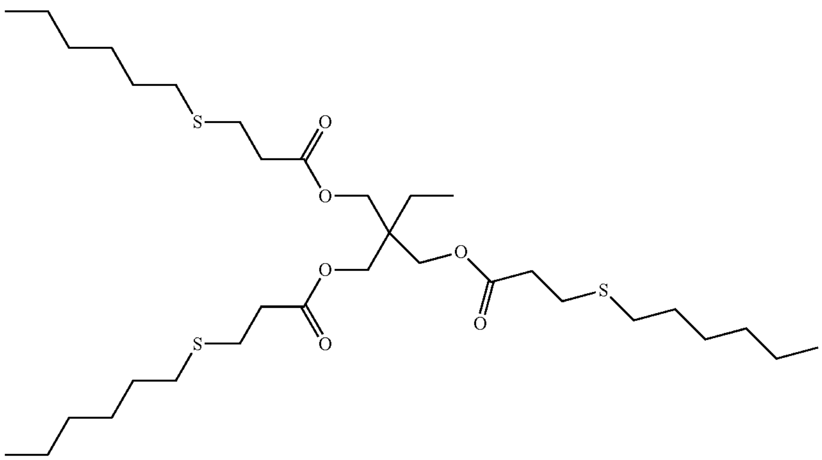
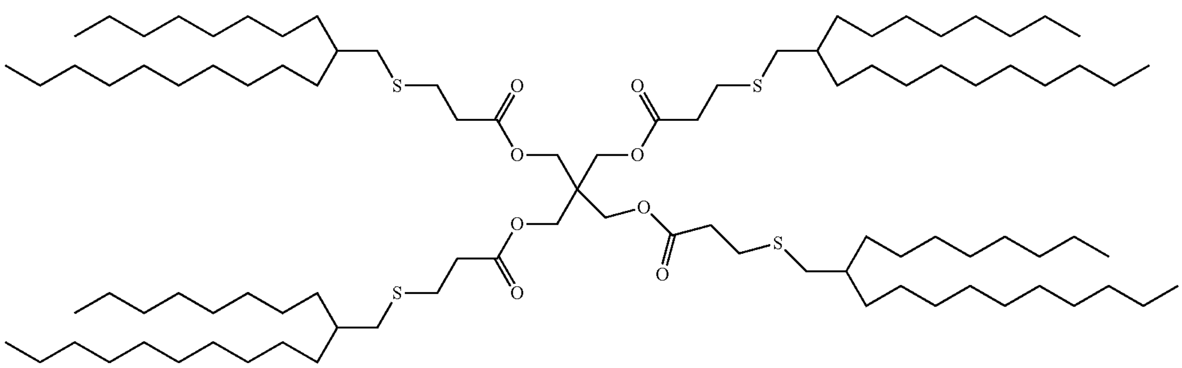
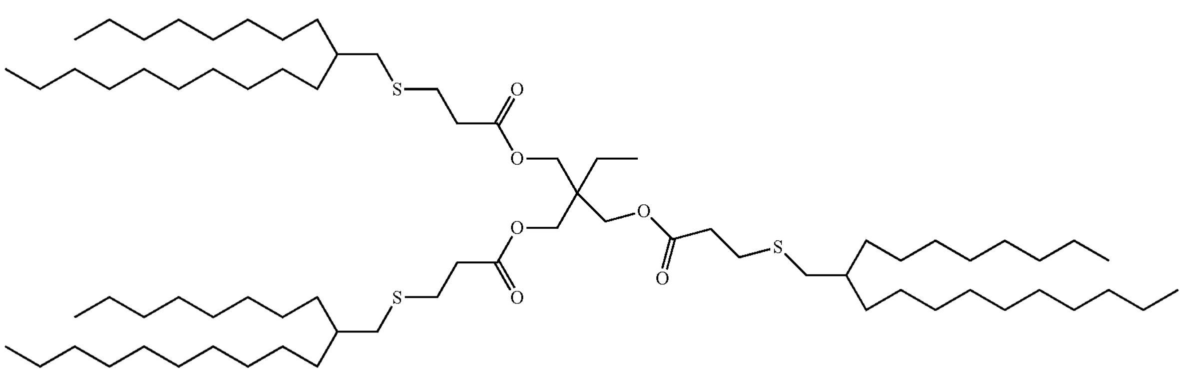


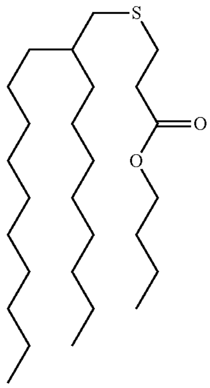


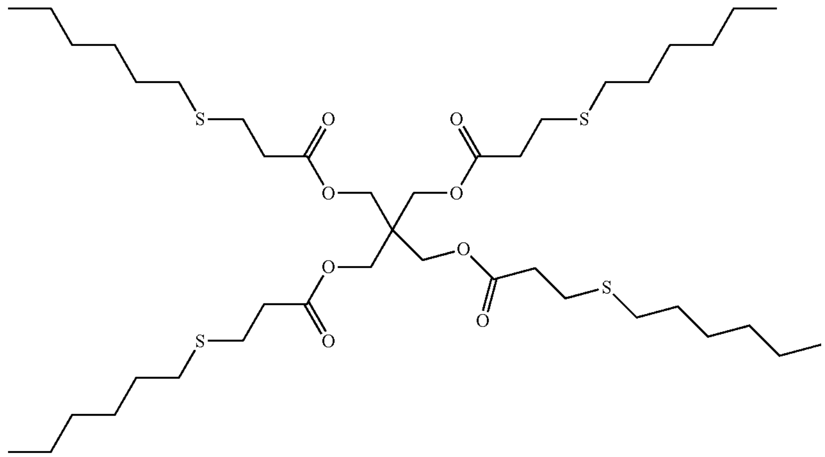


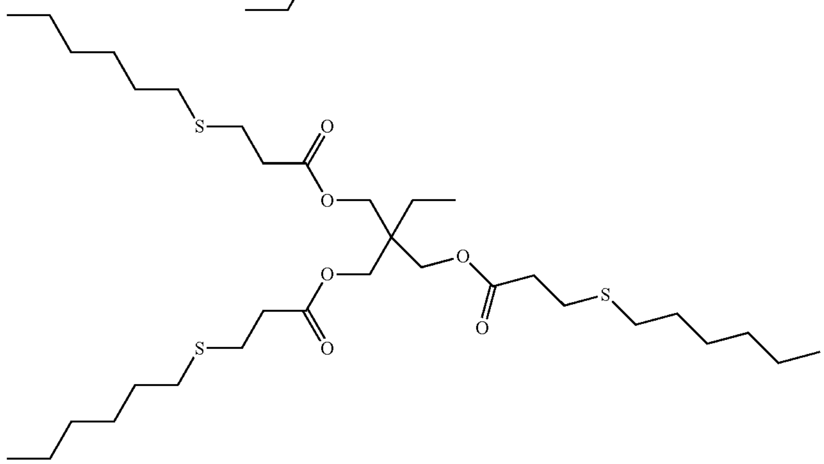
**13**. A lubricating oil comprising a lubricating oil base stock as a major component, and a heteroatom-containing hydrocarbon cobase stock as a minor component; wherein said heteroatom-containing hydrocarbon cobase stock comprises one or more compounds represented by the formula

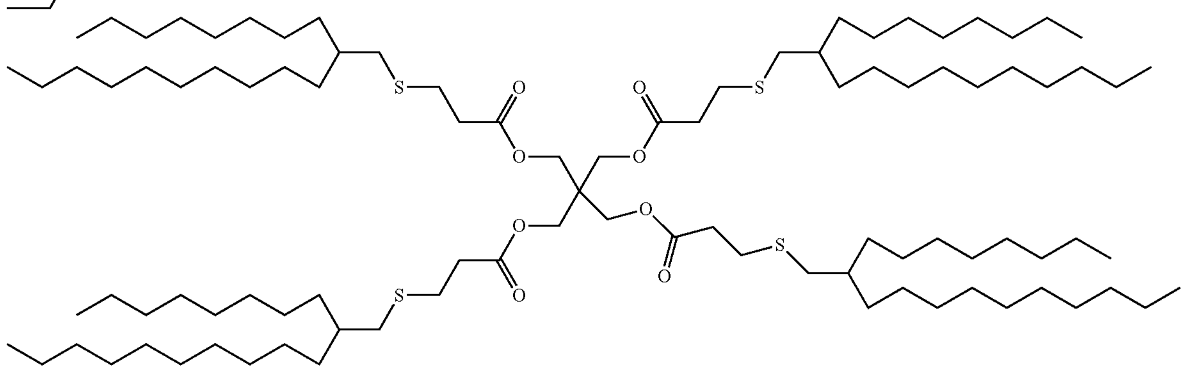
$$(R_1)_a(X)(R_2)_b$$

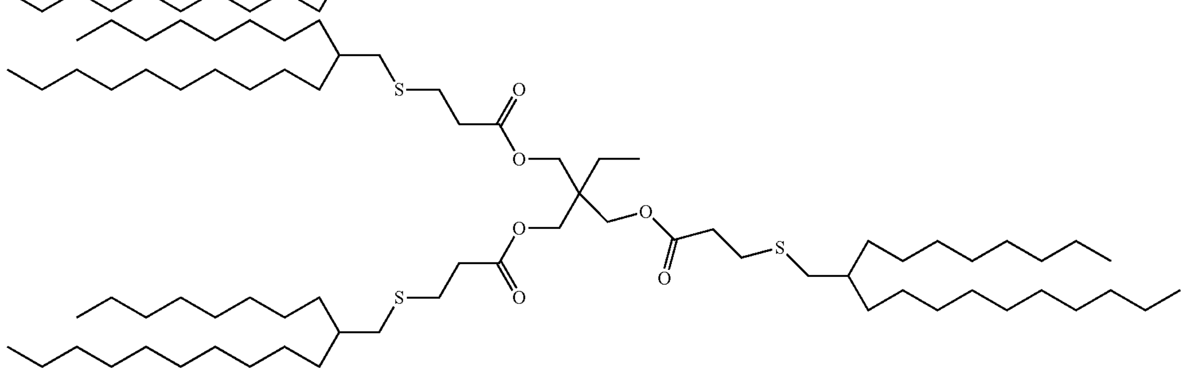
wherein $R_1$ and $R_2$ are the same or different and are the residue of an alkyl group having from 4 to 40 carbon atoms, X is the residue of an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, a is a value from 1 to 6, and b is a value from 0 to 6; wherein said composition has a viscosity ($Kv_{100}$) from 2 to 30 at 100° C., a viscosity index (VI) from 100 to 200, and a Noack volatility of no greater than 20 percent, wherein the heteroatom-containing hydrocarbon cobase stock comprises a heteroatom-containing polyalphaolefin oligomer, or one or more compounds represented by the following formula:











**14**. The lubricating oil of claim **13** wherein the lubricating oil base stock comprises a Group I, II, III, IV or V base oil stock.

**15**. The lubricating oil of claim **13** wherein the lubricating oil base stock comprises a polyalphaolefin (PAO) or gas-to-liquid (GTL) oil base stock.

**16**. The lubricating oil of claim **13** wherein the lubricating oil base stock is present in an amount from 50 weight percent to 99 weight percent, and the heteroatom-containing hydrocarbon cobase stock is present in an amount from 1 weight percent to 50 weight percent, based on the total weight of the lubricating oil.

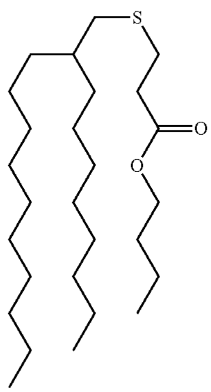
**17**. The lubricating oil of claim **13** wherein the heteroatom-containing hydrocarbon cobase stock is formed from the reaction of a polyalphaolefin dimer, trimer or tetramer with an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol.

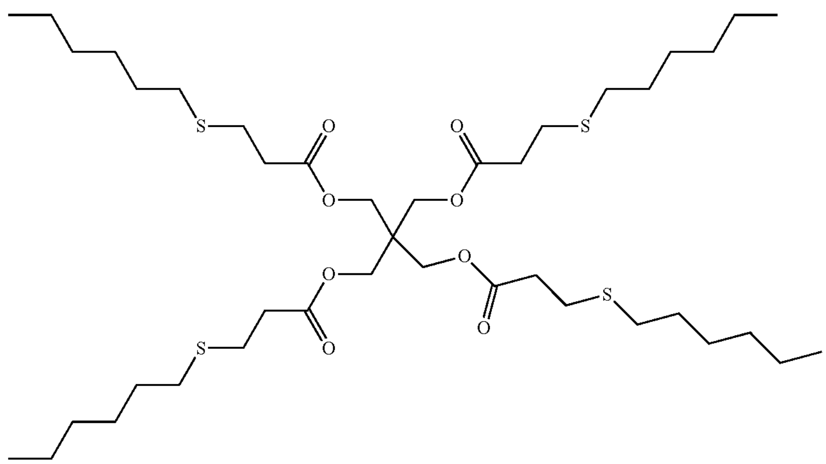
**18**. The lubricating oil of claim **13** wherein the lubricating oil further comprises one or more of a viscosity improver, antioxidant, detergent, dispersant, pour point depressant, corrosion inhibitor, metal deactivator, seal compatibility additive, anti-foam agent, inhibitor, and anti-rust additive.

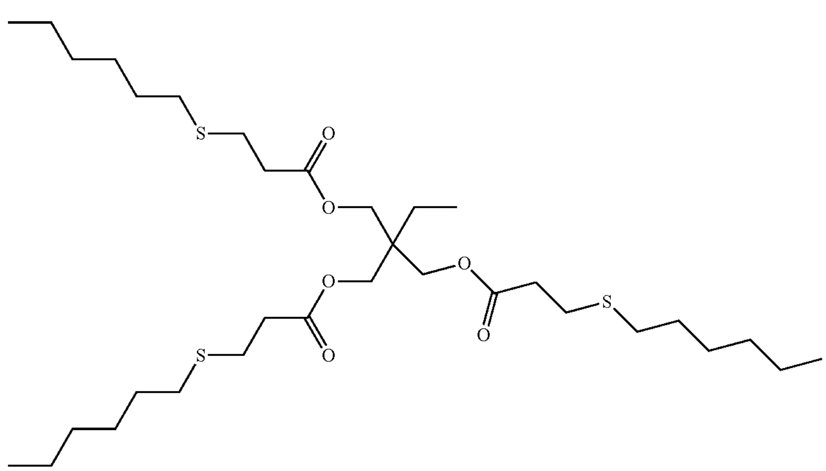
**19**. A method for improving one or more of solubility and dispersancy of polar additives in a lubricating oil by using as the lubricating oil a formulated oil comprising a lubricating oil base stock as a major component, and a heteroatom-containing hydrocarbon cobase stock as a minor component; wherein said heteroatom-containing hydrocarbon cobase stock comprises one or more compounds represented by the formula

$$(R_1)_a(X)(R_2)_b$$

wherein $R_1$ and $R_2$ are the same or different and are the residue of an alkyl group having from 4 to 40 carbon atoms, X is the residue of an aliphatic polythiol, aromatic polythiol, cycloaliphatic polythiol, ester or acid containing thiol, or ester or acid containing polythiol, a is a value from 1 to 6, and b is a value from 0 to 6; wherein said composition has a viscosity ($Kv_{100}$) from 2 to 30 at 100° C., a viscosity index (VI) from 100 to 200, and a Noack volatility of no greater than 20 percent, wherein the heteroatom-containing hydrocarbon cobase stock comprises a heteroatom-containing polyalphaolefin oligomer, or one or more compounds represented by the following formula:







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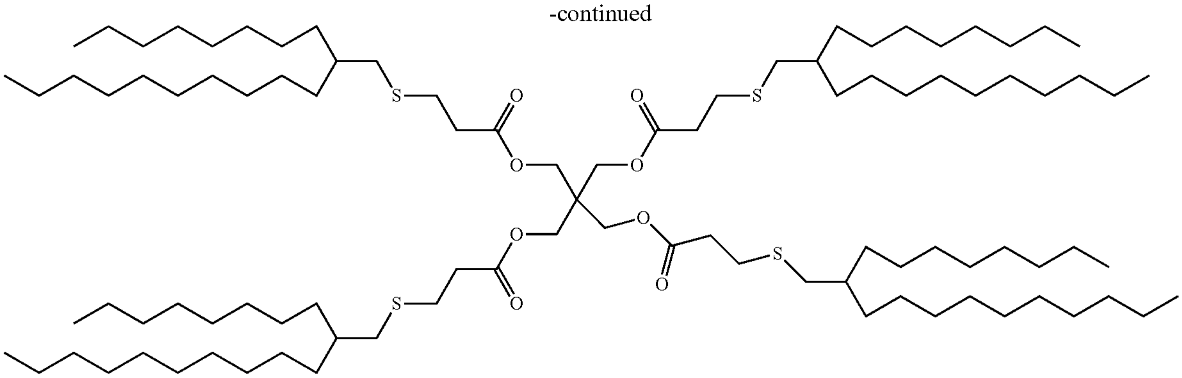

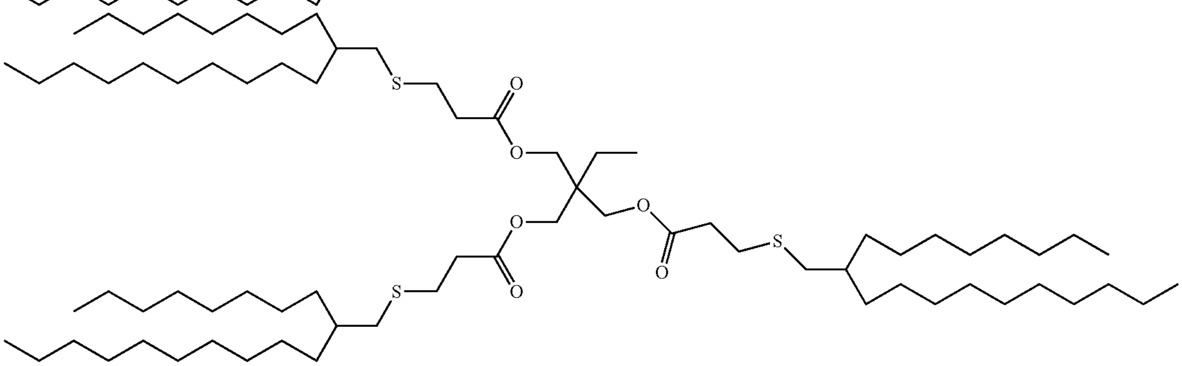

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